Analytical Chemistry by means of Oxalic Acid. II. On the Quantitative Analysis of Barium[1]

By Tamotsu MATSUMOTO

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The methods of precipitating barium as barium oxalate or its various hydrates have been studied by many authors.[2] As to the application of the reaction for determining barium, several investigations[3] have been published, but the results were not effective. The present writer employed 50% alcohol as washing liquid of barium oxalate, and established a method in which barium is estimated gravimetrically as barium oxalate hemihydrate or volumetrically by titrating oxalic acid combined with barium with potassium permanganate.

1. Gravimetric Method.—Procedure:—To 25ml. of hot 0.1 M barium chloride solution which is acidified with dilute hydrochloric acid so that a large quantity of barium oxalate precipitate once formed may be dissolved, a definite quantity of hot 5% ammonium oxalate solution is added with constant stirring. When dilute ammonia water is added drop by drop to the solution until the latter becomes just pink with phenolphthalein, the solution being well agitated all the while, a crystalline precipitate is produced. Now the whole mass in the beaker covered with watch glass is warmed on the water-bath for about 2 hrs., and is left to stand over night. The precipitate after being washed several times by decantation using 50% alcohol solution is filtered with a 1. G. 5. glass filter. Then the precipitate is dried at 100°—105°C. for 2 hrs. in the air-bath, and weighed as barium oxalate hemihydrate.

A) Influences of Amounts of Amm. Oxalate and Dilution of Sample Solution—.In order to find out the most suitable amount of ammonium oxalate which should be taken for the precipitation of barium oxalate and also to learn the influence of dilution of the sample solution, a series of experiments were carried out, the results of which are shown in Table 1.

When the molar ratio of ammonium oxalate to barium exceeds 2.8 and the concentration of the sample solution is less than 0.1 M, the precipitation is not complete. A large quantity of ammonium oxalate seems to form a complex salt of ammonium barium oxalate.[4] So the precipitant should be used in a slight excess, and the sample solution should not be diluted to less than 0.1 M with water.

Table 1

(Ba used is 0.3434 g.)

Water added	5% amm. oxalate		$BaC_2O_4 \cdot 1/2H_2O$	Ba found	Error
ml.	ml.	molar ratio to Ba	g.	g.	mg.
—	10	1.4	0.5860	0.3434	±0
—	20	2.8	0.5858	0.3433	−0.1
—	40	5.6	0.5853	0.3430	−0.4
—	60	8.4	0.5843	0.3424	−1.0
—	80	11.2	0.5834	0.3419	−1.5
25	10	1.4	0.5852	0.3429	−0.5
50	10	1.4	0.5824	0.3413	−2.1
100	10	1.4	0.5805	0.3402	−3.2

Solubilities of Barium Oxalate.—The precipitate of barium oxalate prepared by the above method is dissolved in a solvent, and from the quantity of the precipitate dissolved the solubility of barium oxalate is calculated. Table 2 shows the solubilities of barium oxalate in distilled water as well as in 50% alcohol at 25°—26°C.

Table 2

Solvent	Time that solvent is in contact with ppt. hr.	$BaC_2O_4 \cdot 1/2H_2O$ dissolved in 50 ml mg.	Solubility (25°—26°C) mg./l.	Solubility (25°—26°C) mol/l.	Solubility product
water	8	6.1	121	5.4×10^{-4}	2.9×10^{-7}
	24	6.3			
	32	6.3			
50% alc.	8	trace	3.9	1.7×10^{-5}	2.9×10^{-10}
	24	0.2			
	32	0.2			

From the above results it has been found that the 50% alcohol solution is suitable to the washing

(1) Read before at the 6th Ordinary Meeting of the Chugoku-Shikoku Branch of the Chemical Society of Japan in January, 1952.

(2) A. Souchay and E. Lenssen, *Ann.*, **99**, 36 (1856); Groschuff, *Chem. Ber.*, **34**, 3313 (1901); Herz and Muss, *Chem. Ber.*, **36**, 3718 (1903).

(3) Barbu N. Angelescu, *Bulet. Soc. de Chimie din Romania*, **5**, 12 (1923); J. Haslam, *Analyst*, **60**, 668 (1935), C. Diaz Villamil, *An. Soc. espan. Fizica Quim.*, **34**, 580.

(4) R. Scholder, E. Gadenne and H. Niemann, *Chem. Ber.*, **60**, 1480 (1927).

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of barium oxalate. Moreover the solubility of this salt in water is 3.8×10^{-4} mol/l. (18°C.) according to F. Kohlrausch[5] and 6.8×10^{-4} mol/l. (26°C.) to Herz and Muss.[6]

B) Influence of Various Salts Present.—In order to observe the influence of various salts on the precipitation of barium oxalate, 25 ml. of 0.1 M barium chloride solution was mixed with a definite quantity of various salts, and this solution was treated in the manner described before. The results are shown in Table 3.

Table 3

(Ba used is 0.3434 g.)

Salt mixed	g.	$BaC_2O_4\cdot1/2H_2O$ g.	Ba g.	Error mg.
NaCl	2	0.5857	0.3432	−0.2
〃	〃	0.5859	0.3433	−0.1
KCl	2	0.5859	0.3433	−0.1
〃	〃	0.5860	0.3434	±0
KNO_3	2	0.5858	0.3433	−0.1
〃	〃	0.5859	0.3433	−0.1
NH_4Cl	2	0.5857	0.3432	−0.2
〃	〃	0.5860	0.3434	±0
NH_4NO_3	2	0.5855	0.3431	−0.3
〃	〃	0.5852	0.3429	−0.5
〃	5	0.5825	0.3413	−2.1
〃	〃	0.5830	0.3416	−1.8

Sod. chloride, pot. chloride, pot. nitrate and amm. chloride show almost no bad influence, but amm. nitrate seems to form a complex salt with barium oxalate, which makes the value of barium a little low.

2. Volumetric Method.—J. Haslam[7] studied the titration of the barium oxalate which was formed in perchloric acid solution. The present writer applied the following method to the volumetric analysis of barium.

Procedure:—From a definite volume of 0.1 M barium chloride solution the precipitate of its oxalate is prepared under the best condition required in the former method. When dilute nitric acid is added to the precipitate in a glass filter, oxalic acid is liberated. Then the solution in the filter is filtered out with suction and the filter is well washed with distilled water. All the filtrate is kept in a measuring flask and diluted accurately to 250 ml. 10 ml. of the filtrate, acidified with sulfuric acid, is titrated with 0.1 N potassium permanganate in the usual way. The results are shown in Table 4.

Table 4

Ba taken g.	(0.1M-$BaCl_2$) (ml.)	0.1N-$KMnO_4$ (factor = 0.9479) ml.	Ba found g.	Error mg.
0.3434	(25)	52.65	0.3428	−0.6
0.3434	(25)	52.72	0.3432	−0.2
0.3434	(25)	52.70	0.3431	−0.3
0.1374	(10)	21.08	0.1372	−0.2
0.1374	(10)	21.05	0.1370	−0.4
0.1374	(10)	21.08	0.1372	−0.2
0.0687	(5)	10.52	0.0685	−0.2
0.0687	(5)	10.55	0.0687	±0
0.0687	(5)	10.48	0.0682	−0.5

It has been found that the volumetric analysis by means of oxalic acid produces almost satisfactory results.

Summary

(1) Quantitative precipitation of barium as its oxalate hemihydrate was made possible by employing 50% alcohol as washing solution and by drying the precipitate at 100°—105°C. for 2 hrs.

(2) Sod. chloride, pot. chloride, pot. nitrate and amm. chloride produce little influence on this determination, while amm. nitrate positively effects the estimation.

(3) It was found that barium can be determined volumetrically by titrating with potassium permanganate the oxalic acid which is formed when the barium oxalate is decomposed with nitric acid.

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Chemical Institute, Faculty of Science, Okayama Univ., Osaka

(5) Landolt-Boernstein, "Physik. Chem. Tabellen" (1905 -36).
(6) Herz and Muss, *Chem. Ber.*, **36**, 3718 (1903).
(7) J. Haslam, *Analyst*, **60**, 668 (1936).

On the Vapor Pressure of Liquid Mixture[1]

By Michio KURATA*

(Received May 22, 1952)

Introduction

The theories of "*regular solutions*" were developed by Hildebrand[2] and others[3] with good success in qualitative description of various properties concerning the vapor pressure of liquid mixture. But these theories seem not to be enough for quantitative discussion, especially for the systems exhibiting appreciable departure from "*regular solution*".

In this paper, we shall develop a theory based on the kinetic theory and derive an equation which relates the vapor pressure of a mixture to its composition and the vapor pressures of its constituents. Of course, it is desirable to develop the statistical theory of "*real solutions*", not of "*regular solutions*", because the statistical method gives the most rigorous approach to the problem in question. However, the equation of vapor pressure which results from this approach will come to have a complex form[4], and this is undesirable for the present purpose of deriving a practical equation.

Vapor Pressure of Regular Solution

At first, we will treat of regular solution and confirm that the kinetic method coincides with the statistical method. The treatment of this section corresponds to Penner's method for the vapor pressure of pure liquid[5].

Let us consider the regular solution composed of liquids A and B and denote the molar fractions of each component by x_A and x_B. According to the kinetic theory of gases, the velocities of condensation of each kind of molecule per unit area of surface of the solution, C_A and C_B, may be given by

$$\left.\begin{aligned} & C_A = p_A/(2\pi m_A kT)^{1/2} \\ \text{and} \quad & C_B = p_B/(2\pi m_B kT)^{1/2}, \end{aligned}\right\} \quad (1)$$

where k is the Boltzmann constant and T the absolute temperature. And p_A and p_B represent the partial vapor pressures of the indicated components, m's are the masses of molecule of the indicated species. Here the condensation coefficient is assumed to be unity for simplicity's sake. On the other hand, if we use the theory of absolute rate[6], the velocities of vaporization per unit area, D_A and D_B, are given by

$$\left.\begin{aligned} & D_A = (x_A n)[(kT/h)(F_A^*/F_A)\exp(-\tilde{u}_A/kT)] \\ \text{and} \quad & D_B = (x_B n)[(kT/h)(F_B^*/F_B)\exp(-\tilde{u}_B/kT)], \end{aligned}\right\} \quad (2)$$

Here n is the total number of molecules per unit area, h is the Planck constant and $\tilde{u}_A$ and $\tilde{u}_B$ are the activation energies of vaporization of molecule-A and -B respectively. And F_A (or F_B) represents the partition function of molecule A (or B) at the equilibrium state, F_A^* (or F_B^*) represents the partition function of the activated molecule, which does not include the contribution due to translational motion in the one degree of freedom along the coordinate of vaporization, and they are connected with the free volumes ω_A (or ω_B) and ω_A^* (or ω_B^*) by the familiar relations[7],

$$\left.\begin{aligned} & F_A = (2\pi m_A kT/h^2)^{3/2}\cdot\omega_A \\ \text{and} \quad & F_A^* = (2\pi m_A kT/h^2)\cdot\omega_A^{*2/3} \text{ etc.,} \end{aligned}\right\} \quad (3)$$

respectively. Further, as is shown in Fig. 1 schematically, ω_A^* and ω_B^* can be approximated by the cell volume, v, of the quasi-crystalline lattice or by the volume occupied by one liquid molecule; i. e.

$$\omega_A^* = \omega_B^* = v = (1/n)^{3/2}. \quad (4)$$

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(1) Read at the 2nd Annual Meeting of the Society in April, 1949.

(2) J. H. Hildebrand, "Solubility of Non-electrolytes", New York, 1939.

(3) For example, R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge, 1939, Chap. VIII.

(4) T. S. Chang, (*Proc. Camb. Phil. Soc.*, **35**, 265 (1939)) had treated of liquid mixture of single size molecule and double size molecule.

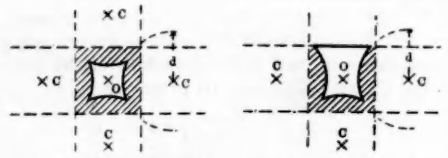
(5) S. S. Penner, *J. Phys. Colloid Chem.*, **52**, 949, 1262 (1948); See also, M. Mizushima, *Kagaku*, **16**, 67 (1946), in Japanese.

(6) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", New York, 1941.

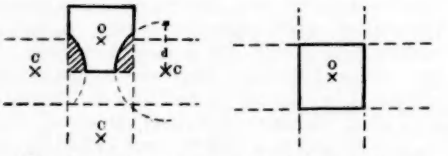
(7) See ref. (6) or ref. (2).

Then Eq. (2) with Eqs. (3) and (4) becomes

$$\left.\begin{aligned} &D_A=x_A(kT/2\pi m_A)^{1/2}(1/\omega_A)\exp(-\tilde{u}_A/kT) \\ &\text{and} \\ &D_B=x_B(kT/2\pi m_B)^{1/2}(1/\omega_B)\exp(-\tilde{u}_B/kT). \end{aligned}\right\} \quad (5)$$



(i) free vol. of liquid molecule, ω. (ii) free vol. of surface molecule.



(iii) free vol. of activated molecule, ω^*. (iv) free vol. of gas molecule, v.

o: center of the molecule whose free volume is in question.
c: center of the adjacent molecules of o-molecule.
d: diameter of molecule.
Shaded area: Region excluded by c-molecules.

Fig. 1.—Schema of free volume.

As the velocities of condensation should be equal to those of vaporization in equilibrium, we put $C_A=D_A$ and $C_B=D_B$ and then obtain

$$\left.\begin{aligned} &p_A=x_A(kT/\omega_A)\exp(-\tilde{u}_A/kT), \\ &p_B=x_B(kT/\omega_B)\exp(-\tilde{u}_B/kT). \end{aligned}\right\} \quad (6)$$

Now if we denote the potential energies of A and B molecules surrounded only by A (or B) molecules by $-u_A$ (or $-u_{AA}$) and $-u_{AB}$ (or $-u_B$), respectively, and use the Bragg-Williams approximation, the total energy U of a solution composed of $N(=N_A+N_B)$ molecules is given by

$$U=N_Au_A+N_Bu_B+2x_Ax_B\cdot N\Delta u \quad (7a)$$

with $$\Delta u\equiv u_{AB}-\{(u_A+u_B)/2\}, \quad (7b)$$

and then $\tilde{u}_A$ and $\tilde{u}_B$ are given by

$$\left.\begin{aligned} &\tilde{u}_A=(\partial U/\partial N_A)_{N_B}=u_A+2x_B^2\Delta u \\ &\text{and} \quad \tilde{u}_B=(\partial U/\partial N_B)_{N_A}=u_B+2x_A^2\Delta u. \end{aligned}\right\} \quad (8)$$

Inserting Eq. (8) into Eq. (6) and putting

$$\left.\begin{aligned} &P_A=(kT/\omega_A)\exp(-u_A/kT) \\ &\text{and} \quad P_B=(kT/\omega_B)\exp(-u_B/kT), \end{aligned}\right\} \quad (9)$$

we can get the well-known formulae

$$\left.\begin{aligned} &p_A=x_AP_A\exp(-2x_A^2\Delta u/kT) \\ &\text{and} \quad p_B=x_BP_B\exp(-2x_B^2\Delta u/kT), \end{aligned}\right\} \quad (10)$$

which coincide with the ones obtained by the statistical method[3]. Of course, P_A and P_B are the vapor pressures of pure liquids A and B respectively. And u_A and u_B are connected with the heats of vaporization, λ_A and λ_B, by

$$\lambda_A=u_A-(kT/2) \text{ and } \lambda_B=u_B-(kT/2). \quad (11)$$

Derivation of Practical Equation for the Total Vapor Pressure, P

In order to take into consideration the difference of sizes between A and B molecules which has been ignored in the preceding section, we should use rather the expression of energy of van Laar's type[8],

$$U-(N_Au_A+N_Bu_B)=\varphi_A\varphi_BB\equiv\Delta U, \quad (12)$$

than Eq. (7). Here φ's are the volume fractions and B is the parameter corresponding to $2N\Delta u$ in Eq. (7). As is well-known, Eq. (12) is derived from the consideration that each molecule is surrounded by A and B molecules in proportion of φ_A and φ_B.

In this paper, we will use the following assumption, instead of Eq. (12), for the purpose of deriving a practical equation.

Assumption.—φ_AN_A molecules of A are surrounded by A molecules only and they have the potential energy of $-u_A$. The remaining φ_BN_A molecules of A are surrounded by B molecules only and they have the potential energy of $-u_{AB}$. Similarly, φ_AN_B molecules of B and the remaining φ_BN_B have the potential energies of $-u_{AB}$ and $-u_B$ respectively.

Using this assumption and denoting the free volume of a molecule surrounded by the molecules of different species only by ω_{AB}, we get

$$\left.\begin{aligned} &D_A=x_A(kT/2\pi m_A)^{1/2}[(\varphi_A/\omega_A)\cdot \\ &\exp(-u_A/kT)+(\varphi_B/\omega_{AB})\exp(-u_{AB}/kT)], \\ &D_B=x_B(kT/2\pi m_B)^{1/2}[(\varphi_A/\omega_{AB}) \\ &\exp(-u_{AB}/kT)+(\varphi_B/\omega_B)\exp(-u_B/kT)]. \end{aligned}\right\} \quad (13)$$

These equations correspond to Eq. (5) for regular solution.

(8) J. J. van Laar, *Z. phys. Chem.*, **A 137**, 421 (1928).

Now let us define the "mutual vapor pressure" P_{AB} by the similar relation as Eq. (9),

$$P_{AB}=(kT/\omega_{AB})\exp(-u_{AB}/kT). \quad (14)$$

Then, equating Eqs. (1) and (13) and using Eqs. (9) and (14), we can easily obtain

$$\left.\begin{aligned} p_A&=x_A\varphi_A P_A+x_A\varphi_B P_{AB} \\ \text{and}\quad p_B&=x_B\varphi_A P_{AB}+x_B\varphi_B P_{\circ\circ}. \end{aligned}\right\} \quad (15)$$

For practical purposes, we may put

$$x_A\varphi_B+x_B\varphi_A=2(x_Ax_B\varphi_A\varphi_B)^{1/2}, \quad (16)$$

obtaining our final result,

$$P=p_A+p_B=x_A\varphi_A P_A+x_B\varphi_B P_B +2(x_Ax_B\varphi_A\varphi_B)^{1/2}P_{AB}. \quad (17)$$

Comparison of Eq. (17) with the Experimental Data

To make comparison of Eq. (17) with the experimental values, we must evaluate P_{AB}, which is the sole unknown parameter in the equation. In this section, we will use for P_{AB} the value evaluated from the observed value of P, P_{obs}, at a composition $x_A \fallingdotseq x_B$.

Table 1

List of the Systems Compared and the Results Obtained.—I.

System (Ref.*)	°C.	P_{AB}	$\bar{\Delta}$, %
$CCl_4+C_6H_6$ (i)	0	33.3	0.3
	10	58.0	0.3
	20	90.5	0.2
	30	138.0	0.1
	40	206.5	0.1
$CS_2+C_6H_6$ (ii)	0	120.0	2.2
	10	177.0	2.2
	20	263	2.0
	30	380	1.3
	40	530	1.3
$CCl_4+C_2H_5OH$ (i)	34.8	328	3.4
	50	626	3.5
	60	928	3.7
	66	1162	3.9
$CCl_4+C_6H_5CH_3$ (ii)	10	40.8	0.8
	20	60.5	1.1
	30	94.7	1.3
	40	138.0	0.8
	50	210.5	0.5
	60	304	0.5
	70	420	0.4
CS_2+CHCl_3 (ii)	0	141.0	1.4
	10	217	1.4
	20	322	1.7
	30	467	1.0
	40	660	0.9
$CS_2+CH_3COCH_3$ (ii)	0	235	5.9
	10	371	5.3
	20	557	4.5
	30	817	3.8
	35	960	3.6
$CS_2+C_6H_5CH_3$ (ii)	10	147	4.3
	20	222	4.0
	30	324	3.5
	40	460	1.8
$C_6H_6+CHCl_3$ (ii)	0	45.4	0.6
	20	122.5	1.1
	40	266	0.3
	60	574	0.2
$C_6H_6+CH_3OH$ (ii)	0	81.9	5.6
	10	144.0	5.4
	20	236	4.9
	30	379	5.5
	40	590	6.7
	60	1300	7.8
$C_6H_6+CH_3COOH$ (ii)	20	95.0	2.2
	30	157.0	2.8
	40	239	4.0
	50	357	3.2
	60	520	3.0
	70	737	2.0
$C_6H_6+C_2H_5OH$ (i)	34.8	288	5.0
	50	557	5.3
	60	830	5.5
	66	1057	5.8
$C_6H_6+n\text{-}C_3H_7OH$ (ii)	10	63.0	8.4
	20	106.0	6.3
	30	172.0	5.7
	40	270	5.5
	50	410	6.4
$C_6H_6+C_2H_5OC_2H_5$ (ii)	0	98.0	0.4
	10	157.0	0.4
	20	242	0.2
	30	347	0.3
$C_6H_6+CH_3CO_2C_2H_5$ (ii)	10	84.5	3.3
	20	138.3	0.9
	30	214	1.3
	40	330	1.4
	50	466	1.4
	60	657	1.1
$C_6H_6+C_6H_5CH_3$ (ii)	10	34.7	1.6
	20	59.4	1.1
	30	98.5	0.9
	40	149.0	1.1
	50	214	0.9
	60	303	0.4
	80	574	0.5

* References:

(i) *International Critical Tables*, Vol. III, pp. 285, 358 (1928).
(ii) Schmidt, *Z. Phys. Chem.*, **121**, 221 (1926).

The comparison of P_{calc} with P_{obs} has been performed in regard to about 20 systems which are chosen from various types of mixtures as shown in Tables 1 and 2. In these tables are arranged the systems in three classes: mixtures of (A) non-polar and non-polar liquids, (B) non-polar and polar liquids and (C) polar and polar liquids, for convenience's sake. In these tables are also tabulated P_{AB} in terms of mm. Hg and $\overline{\Delta}$ which is the arithmetical mean of $|P_{calc}-P_{obs}|\times 100/P_{obs}$ at various compositions. $\overline{\Delta}$ is regarded as a kind of measure of the coincidence of P_{calc} with P_{obs}. Some of the results of calculations are plotted in Figs. 2 and 3, where the circles and the full lines represent the observed and the calculated values respectively. The agreement of P_{calc} with P_{obs} seems to be fairly good for all of the systems listed in Tables 1 and 2.

Table 2

List of the Systems Compared and the Results Obtained.—II.

System (Ref.*)	°C.	P_{AB}	$\overline{\Delta}$, %
H_2O+CH_3OH (i)	39.9	165	3.3
	59.4	416	2.8
$H_2O+C_2H_5OH$ (i)	40	159	4.4
	55	338	4.4
	75	823	4.2
$H_2O+n\text{-}C_3H_7OH$ (i)	30.3	83.0	3.7
	49.9	240	4.9
	65.9	510	4.2
	79.8	930	3.7
$CHCl_3+CH_3COCH_3$ (ii)	0	43.8	0.9
	10	65.2	2.1
	20	112.3	1.9
	30	178	2.0
	40	270	1.7
	50	395	1.5
$CHCl_3+C_2H_5OC_2H_5$ (ii)	0	86.4	2.2
	10	135.0	1.0
	20	213	0.6
	30	309	0.3
$CH_3OH+C_2H_5OH$ (ii)	10	41.6	1.4
	20	74.2	0.4
	30	134.0	0.7
	40	215	0.2
	50	345	0.3
	60	528	0.4
$CH_3OH+n\text{-}C_3H_7OH$ (ii)	10	40.6	0.6
	20	72.5	1.3
	30	134.0	0.3
	40	217	0.8
	50	346	0.6
	60	495	0.5
$C_2H_4Br_2+C_2H_6Br_2$ (i)	85.1	152.0	0.4
$C_2H_5OH+C_2H_5CO_2H_5$ (i)	0	173	5.6
	10	269	5.0
	20	405	4.6
	30	594	3.9
	35	713	4.0
CH_3COCH_3	20	432	0.7
$+C_2H_5OC_2H_5$ (i)	30	642	1.4
$CH_3CO_2C_2H_5$	0	109.0	0.3
$+C_2H_5OC_2H_5$ (ii)	10	167.0	0.2
	20	258	0.2
	30	388	0.8

* References are given in Table 1.

Further, if we plot log P_{AB} against $1/T$, a straight line will be obtained according to the definition of P_{AB}, Eq. (14). That is, defining the "mutual heat of vaporization", λ_{AB}, by

$$\lambda_{AB}=u_{AB}-(kT/2), \tag{18}$$

and putting

$$b=\lambda_{AB}/2.303\,k, \tag{19}$$

we can write Eq. (14) in the form,

Table 3

Values of a and λ_{AB}.

System A	System B	a	b	λ_{AB}	$(\lambda_A+\lambda_B)/2$	$\lambda_A(\lambda_B)$*
				(kcal./mole)		
CCl_4	C_6H_6	7.720	1691	7.74	7.77	7.67
CS_2	C_6H_6	7.265	1420	6.50	7.25	6.65
CCl_4	EtOH	8.490	1840	8.42	8.83	
CCl_4	$PhCH_3$	7.600	1705	7.80	7.96	(8.24)
CS_2	$CHCl_3$	7.388	1431	6.55	7.03	
CS_2	Me_2CO	7.672	1445	6.61	7.17	
CS_2	$PhCH_3$	7.335	1463	6.69	7.44	
C_6H_6	$CHCl_3$	7.850	1694	7.75	7.64	7.86
C_6H_6	MeOH	8.590	1823	8.34	8.43	
C_6H_6	AcOH	8.096	1792	8.20	8.73	(9.60)
C_6H_6	EtOH	8.671	1915	8.76	8.93	
C_6H_6	PrOH	8.396	1868	8.55	9.48	(11.10)
C_6H_6	Et_2O	7.766	1578	7.22	7.31	
C_6H_6	AcOEt	7.875	1682	7.70	8.15	
C_6H_6	$PhCH_3$	7.714	1742	7.97	8.05	
H_2O	MeOH	9.063	2143	9.81	9.65	10.30
H_2O	EtOH	9.316	2228	10.19	10.15	
H_2O	PrOH	9.411	2273	10.40	10.70	
$CHCl_3$	Me_2CO	7.850	1698	7.77	7.56	7.42
$CHCl_3$	Et_2O	7.538	1530	7.00	7.08	(6.75)
MeOH	EtOH	8.962	2077	9.50	9.50	9.00
MeOH	PrOH	9.114	2125	9.72	10.05	
EtOH	Et_2O	7.648	1478	6.76	8.37	10.00
Me_2CO	Et_2O	7.847	1528	6.99	7.23	7.70
AcOEt	Et_2O	7.632	1530	7.00	7.60	8.45

* Values in parentheses are the heat of vaporization of B-component given in the same row.

$$\log_{10} P_{AB} = a - (b/T), \qquad (20)$$

to a good approximation. The demand for this linearity is, indeed, satisfied by the values of P_{AB} tabulated in Tables 1 and 2. In Table 3 are given the values of a and b in Eq. (20). Using these values, we can obtain P_{AB} at any temperature. In this Table, are also tabulated λ_{AB} in terms of kcal./mole and, for comparison's sake, $(\lambda_A+\lambda_B)/2$ and λ_A (or λ_B). It should be noticed that the signs of $\Delta\lambda$ defined by

$$\Delta\lambda = \lambda_{AB} - \{(\lambda_A+\lambda_B)/2\} = \Delta u \qquad (21)$$

are consistent with the sign of the heat of mixing for all of the systems cited here. Especially,

$$\Delta\lambda = (6.99-7.23) = -0.24 \text{ kcal./mole}$$

for the mixture of acetone and ethyl ether, which is regarded as "regular solution", coincides with the value of Δu evaluated by Porter[9] from Eq. (10), $2\Delta u/kT = -0.741$ at 30°C., quantitatively. These results are to be compared with the fact that the sign of Δu evaluated by Eq. (10) conflicts some times with the one expected from the heat of mixing for the system exhibiting appreciable departure from regular solution (for example, H_2O+CH_3OH). And λ_{AB} obtained from the present method is consistent with the value of "activation energy of flow" estimated from the data of the viscosity coefficient as was illustrated in our previous paper[10].

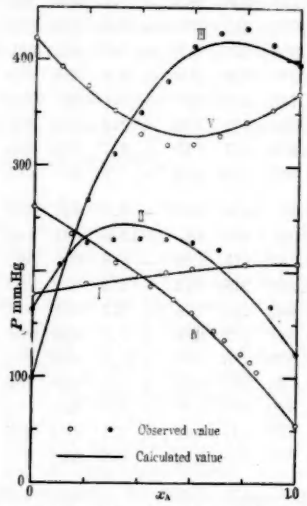


Fig. 2.—Observed and calculated values of P–1: Curve I, A=CCl_4, B=C_6H_6 (40°C.); Curve II, A=C_6H_6, B=CH_3OH (30°C.); Curve III, A=C_6H_6, B=CH_3COOH (60°C.); Curve IV, A=H_2O, B=CH_3OH (39.9°C.); Curve V, A=$CHCl_3$, B=CH_3COCH_3 (40°C).

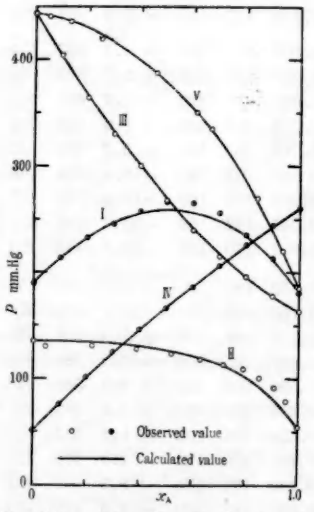


Fig. 3.—Observed and calculated values of P–2: Curve I, A=C_6H_6, B=$CH_3CO_2C_2H_5$ (40°C.); Curve II, A=H_2O, B=C_2H_5OH (40°C.); Curve III, A=$CHCl_3$, B=$C_2H_5OC_2H_5$ (20°C.); Curve IV, A=CH_3OH, B=n-C_3H_7OH (40°C.); Curve V, A=CH_3COCH_3, B=$C_2H_5OC_2H_5$ (20°C.).

However, our formula for the partial vapor pressure shows, unfortunately, only poor agreement with the experimental data. So, we cannot calculate the so-called "x to y diagram" (diagram of the composition of solution to that of vapor) from the present theory.

Estimation of $\Delta\lambda$ from Heat of Mixing

In this section, we will compare λ_{AB} or $\Delta\lambda$ given in Table 3 with those estimated from the heat of mixing, ΔH.

As the difference between H (enthalpy) and U (energy) can be neglected in liquid phase, we get from Eqs. (12) and (21)

$$\Delta H \equiv \Delta U = 2\varphi_A\varphi_B(N\Delta\lambda), \qquad (22)$$

where plus sign of ΔH represents the heat evolved by the solution. Using this relation, we can again estimate $\Delta\lambda$ from the observed values of ΔH. In Table 4 are given the results of calculation for some examples.

Though the constancy of $\Delta\lambda$ to x_A is not enough in examples 2 or 3, the values of $\Delta\lambda$ thus estimated will give, at least, their correct

(9) A. W. Porter, *Trans. Farad. Soc.*, **16**, 336 (1920).
(10) M. Tamura and M. Kurata, This Bulletin, **25**, 32 (1952), Eq. (17) and Table 3.

order. As the values of $\Delta\lambda$ obtained from Table 3 are in agreement with the ones estimated here within small error, 50~60 cal./mol., we can conclude that λ_{AB} tabulated in Table 3 gives the correct measure of energy of molecular contact of A−B type within small error, probably less than 0.1 kcal./mole (or less than 2%).

Table 4

Estimation of $\Delta\lambda$ from Heat of Mixing.

Example 1. A=CCl_4, B=C_6H_6 at 25°C.

x_A	ΔH kjoule/mole	$\Delta\lambda$ kcal./mole Eq. (22)	$\Delta\lambda$ kcal./mole Table 3
0.300	−0.091	−0.050	
0.351	−0.106	−0.054	
0.501	−0.107	−0.051	−0.03
0.618	−0.104	−0.053	
0.731	−0.089	−0.056	

Example 2. A=C_6H_6, B=C_2H_5OH at 15°C.

x_A	ΔH joule/g. soln.	$\Delta\lambda$ kcal./mole Eq. (22)	$\Delta\lambda$ kcal./mole Table 3
0.202	−6.067	−0.194	
0.282	−6.867	−0.197	
0.469	−7.556	−0.230	−0.17
0.579	−7.338	−0.264	
0.702	−6.706	−0.331	

Example 3. A=C_6H_6, B=$CHCl_3$ at 18°C.

x_A	ΔH joule/g. soln.	$\Delta\lambda$ kcal./mole Eq. (22)	$\Delta\lambda$ kcal./mole Table 3
0.219	2.64	0.170	
0.396	3.31	0.160	
0.496	3.31	0.157	0.11
0.604	3.18	0.160	
0.723	2.89	0.178	

Data of ΔH are adopted from "*International Critical Tables*" Vol. V, p. 154.

Table 5

Total Vapor Pressure of the Mixture of CCl_4 (A), C_2H_5OH (B) and C_6H_6 (C).

x_A	x_B	34.8°C. $P_{obs.}$	34.8°C. P_{calc}	34.8°C. Δ, %	60°C. $P_{obs.}$	60°C. P_{calc}	60°C. Δ, %
0.131	0	153	153	0	407	404	− 0.7
0.126	0.040	191	161	−15.7	515	431	−16.3
0.112	0.144	201	181	− 9.9	559	492	−12.0
0.094	0.288	204	200	− 2.0	580	556	− 4.1
0.078	0.408	204	209	+ 2.5	585	591	+ 1.0
0.058	0.561	199	208	+ 4.5	577	603	+ 4.5
0.045	0.661	193	199	+ 3.1	564	588	+ 4.3
0.035	0.736	186	188	+ 1.1	546	562	+ 2.9
0.022	0.833	167	165	− 1.2	508	509	+ 0.2
0.013	0.900	143	144	+ 0.7	462	457	− 1.1
0.007	0.945	130	127	− 2.3	421	415	− 1.4
0.386	0	163	162	− 0.6	426	426	0
0.363	0.061	203	175	−13.8	551	466	−15.4
0.342	0.116	208	185	−11.1	575	499	−13.2
0.289	0.253	212	205	− 3.3	599	564	− 5.8
0.232	0.400	212	217	+ 2.3	603	611	+ 1.3
0.178	0.540	208	216	+ 3.8	598	619	+ 3.5
0.100	0.742	190	192	+ 1.1	560	572	+ 2.1
0.058	0.850	167	163	− 2.4	508	506	− 0.4
0.035	0.909	147	143	− 2.7	465	455	− 2.2
0.019	0.951	128	126	− 1.6	417	415	− 0.5
0.587	0	166	167	− 0.6	435	436	+ 0.2
0.550	0.063	207	181	−12.6	561	480	−14.4
0.501	0.147	215	196	− 8.8	600	532	−11.3
0.432	0.266	218	212	− 2.8	612	583	− 4.7
0.329	0.440	216	224	+ 3.7	615	632	+ 2.8
0.269	0.542	213	221	+ 3.8	608	634	+ 4.3
0.190	0.675	203	207	+ 2.0	588	608	+ 3.4
0.134	0.773	187	188	+ 0.5	559	566	+ 1.3
0.094	0.839	173	170	− 1.7	522	519	− 0.6
0.045	0.921	144	141	− 2.1	459	448	− 2.4
0.013	0.978	115	114	− 0.9	387	382	− 1.3
0.745	0	170	170	0	441	442	+ 0.2
0.538	0.277	221	218	− 1.4	625	596	− 4.6
0.420	0.436	219	227	+ 3.7	624	637	+ 2.1
0.323	0.566	215	223	+ 3.7	615	640	+ 4.1
0.204	0.726	199	202	+ 1.5	583	595	+ 2.1
0.141	0.811	184	180	− 2.2	543	548	+ 0.9
0.093	0.875	163	160	− 1.8	497	496	− 0.2
0.045	0.940	137	133	− 2.9	437	429	− 1.8
0.497	0.503	223	232	+ 4.0	637	655	+ 2.8
0.416	0.421	220	226	+ 2.7	628	633	+ 0.8
0.357	0.361	217	220	+ 1.4	617	612	− 0.8
0.284	0.288	213	209	− 1.9	602	579	− 3.8
0.215	0.218	209	197	− 5.7	589	542	− 8.0
0.139	0.141	201	180	−10.4	566	489	−13.6
0.083	0.085	194	169	−12.9	535	455	−14.9
0.041	0.042	182	158	−13.2	490	411	−16.1
0.018	0.019	170	152	−10.6	446	404	− 9.4
0.190	0.810	187	185	− 1.1	554	558	+ 0.7
0.178	0.760	194	194	0	571	576	+ 0.9
0.168	0.717	199	201	+ 1.0	581	593	+ 2.1
0.157	0.669	202	206	+ 2.0	586	603	+ 2.9
0.139	0.590	205	212	+ 3.4	589	615	+ 4.4
0.114	0.486	205	214	+ 4.4	589	611	+ 3.7
0.079	0.334	203	205	+ 1.0	583	573	− 1.7
0.052	0.221	200	191	− 4.5	570	526	− 7.7
0.033	0.140	194	176	− 9.3	548	481	−12.2
0.013	0.057	185	160	−13.5	509	429	−15.7
0.006	0.027	172	154	−10.5	457	408	−10.7

	P_A	P_B	P_C	P_{AB}	P_{BC}	P_{AC}
34.8°C.	173	103	147	328	288	170
60°C.	446	354	389	928	830	443

Data of $P_{obs.}$ are adopted from Ref. (i) in Table 1.

Total Vapor Pressure of Ternary Liquid Mixture

Extending the treatment mentioned above to ternary mixture of liquids composed of *A*, *B* and *C* components, we can easily obtain the relation having the similar type to Eq. (17);

$$P=x_A\varphi_A P_A+x_B\varphi_B P_B+x_C\varphi_C P_C +2(x_A x_B\varphi_A\varphi_B)^{1/2}P_{AB}+2(x_B x_C\varphi_B\varphi_C)^{1/2}P_{BC} +2(x_C x_A\varphi_C\varphi_A)^{1/2}P_{AC}. \quad (23)$$

Then, if we know P_{obs} at least at three compositions, for example, (i) $x_A=x_B=1/2$, (ii) $x_B=x_C=1/2$ and (iii) $x_A=x_C=1/2$, it will be possible to calculate P at any composition. In Table 5 are given the results of calculation for the system, carbon tetrachloride+benzene +ethyl alcohol. The degree of agreement of P_{calc} with P_{obs} is the same order as the one obtained for the binary mixture. The values of P_A, P_B, P_C, P_{AB}, P_{BC} and P_{AC} used in this calculation are tabulated in the last part of this table. Among these values, P_{AB} and P_{BC} were already given in Table 1 and P_{AC} was calculated by Eq. (20) with a and b given in Table 3.

It seems to be a strong point of the present method that the extension to the multi-component system can be performed very easily as shown here.

Summary

(1) The kinetic method was applied to the vapor pressure of regular solution; the result being in agreement with that of the statistical method.

(2) New semi-empirical equations having simple form were derived for the vapor pressures of binary and ternary mixtures of liquids and satisfactory agreements of these equations with the experimental data were illustrated in regard to about 20 examples.

In conclusion the author wishes to express sincere thanks to Professor Mikio Tamura for his kind guidance throughout this work. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education.

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Ultraviolet Absorption Spectra of Troponoids[1]

By Masamichi TSUBOI

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Introduction

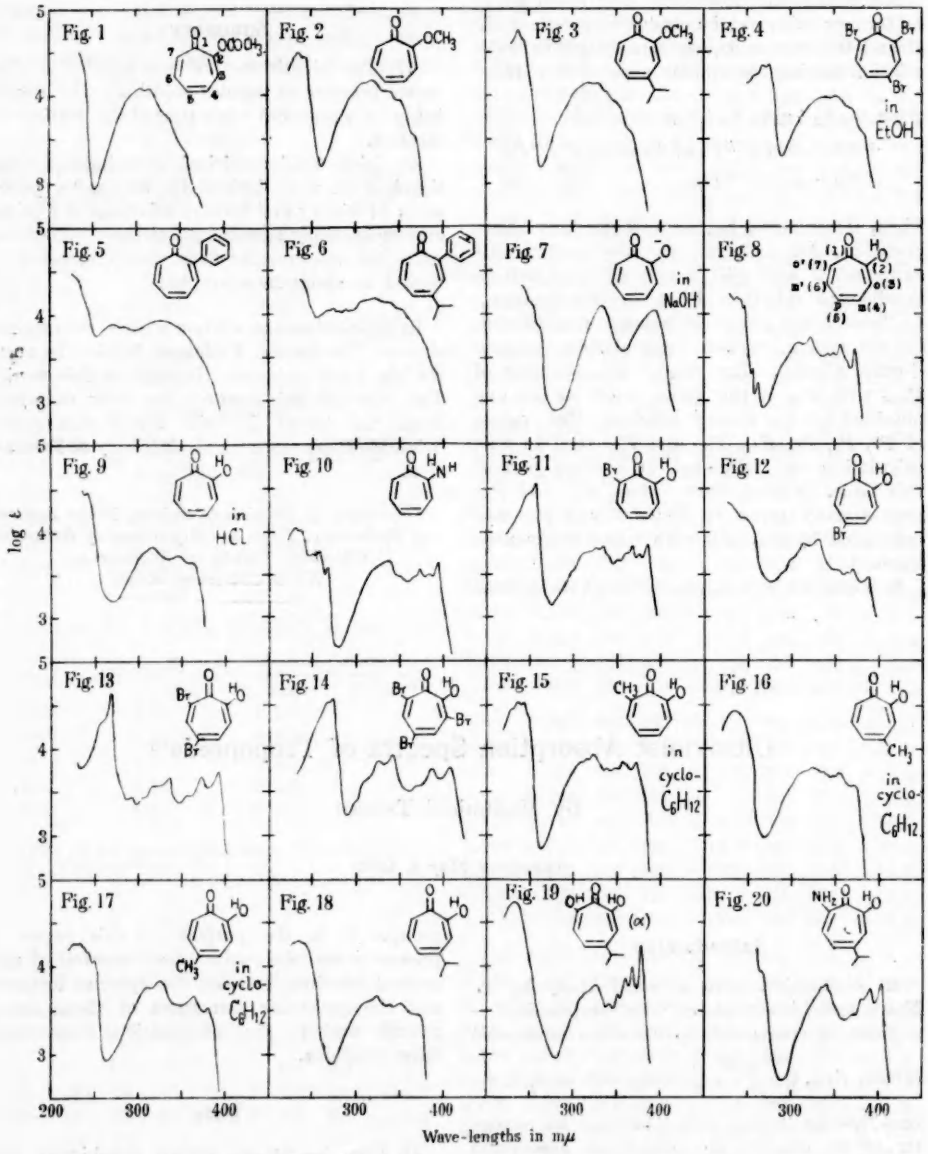
In connection with a serial study by T. Nozoe and his coworkers[2] on "troponoids"—a group of compounds with a seven-membered carbon ring, (cycloheptatriene-2, 4, 6-one-1),—the present writer has had an opportunity to observe the ultraviolet absorption spectra of more than twenty compounds of this group. It is the purpose of this paper to present what the writer has observed of the general relations between the spectral features and the molecular structures of these compounds and to give explanations concerning these relations.

Data

In Figs. 1—20 are shown graphically the data of the ultraviolet absorption spectra of troponoids, as obtained by means of a Beckman spectrophotometer model DU. Samples used are listed in Table 1, with remarks on them. All of these samples were prepared by Nozoe and his co workers. The structural formulas of most of these compounds were determined

(1) T. Nozoe and his co-workers give the general name "troponoids" to tropone, tropolone, and related compounds.

(2) T. Nozoe, *Sci. Rep. Tohoku Univ.*, Ser. I, **34**, 199 (1950); *Nature*, **167**, 1056 (1951); *Chem and Chem. Industry (Chem. Soc. Japan)*, **4**, 348 (1951).



Figs. 1—20.—Ultraviolet Absorption Spectra of Troponoids
(Solvent: iso octane unless otherwise stated)

Table 1

Substances	Melting Points, °C.	References	Structural Formulas and Ultraviolet Absorption Spectra
Tropolone acetate	69.5-70.5	(3)	Cf. Fig. 1
Tropolone methyl ether	(oil)	(4)	Cf. Fig. 2
Hinokitiol methyl ether	(oil)	(5)	Cf. Fig. 3
2, 4, 7-Tribromotropone	185	(6)	Cf. Fig. 4
2-Phenyltropone	85-86	(7)	Cf. Fig. 5
2-Phenyl-4-(or 6)-isopropyl-tropone	93-94	(7)	Cf. Fig. 6
Tropolone	50-51	(8)	Cf. Figs. 7, 8 and 9
2-Aminotropone	106-107	(9)	Cf. Fig. 10
o-Bromotropolone	107-108	(8) and (10)	Cf. Fig. 11
p-Bromotropolone	190-191	(8)	Cf. Fig. 12
o, *p*-Dibromotropolone	152-153	(10)	Cf. Fig. 13
o, *o'*, *p*-Tribromotropolone	125-126	(8)	Cf. Fig. 14
o-Methyltropolone	51	(11)	Cf. Fig. 15
m-Methyltropolone	76	(12)	Cf. Fig. 16
p-Methyltropolone	110	(5)	Cf. Fig. 17
Hinokitiol (*β*-Thujaplicin) (*m*-Isopropyl-tropolone)	51-52	(13)	Cf. Fig. 18
o'-Hydroxyhinokitiol	60(α), 52(β), 46(γ)	(14)	Cf. Fig. 19(α)
o'-Aminohinokitiol	99	(15)	Cf. Fig. 20

also by them.[3]~[15] In the present experiments, iso-octane was used as the solvent in most cases, but in the cases where the measurements corresponding to Figs. 4, 7, 9, and 15—17 were made, ethanol, NaOH solution, HCl solution, and cyclohexane were used respectively as the solvents.

Discussion

I. General Features.—Each of the absorption spectra of troponoids so far observed is divisible, without exception, into two parts—one ranging from 200 to 300 mμ which is composed of the absorption bands with ε-values of 10^4-10^5, and the other ranging from 300 to 400 mμ which is composed of the absorption bands a little weaker in intensity ($\varepsilon = 10^3$-10^4). This is a characteristic feature common to all the troponoids spectra.

In detail, however, the spectra of troponoids may be classified into two types:

Type A (Tropone type)—This is represented by the spectrum of tropone, which shows only one electronic band in the 300-400 mμ region.[16] The spectra of Figs. 1—6 belong to this type. All of these spectra are of tropone derivatives with no hydrogen bonds.

Type B (Anion type)—This is represented by the spectrum of tropolone anion (Fig. 7), which is observed when tropolone is dissolved in an alkaline solution. Each of the spectra of this type shows two electronic bands in the 300-400 mμ region. The spectra of Figs. 8—20 belong to this type. All of these spectra are of tropone derivatives which have either OH or NH_2 radical on the 2-carbon atom (C_2) (carbon atom adjacent to the carbonyl carbon atom) and an intramolecular hydrogen bond between the OH or NH_2 and the carbonyl oxygen atom.

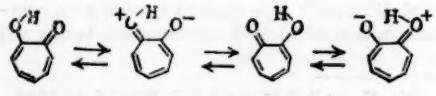
All the compounds examined have C=O and C=C's conjugated with each other. According to McMurry,[17] it is expected, with such compounds, that two kinds of electronic bands will

(3) T. Nozoe, S. Seto, and T. Sato, to be published.
(4) T. Nozoe, S. Seto, T. Ikemi, and T. Arai, *Proc. Japan Acad.*, **27**, 102 (1951).
(5) T. Nozoe, *Science of Drugs*, **3**, 171 (1949).
(6) T. Nozoe, Y. Kitahara, T. Ando, and S. Masamune, *Proc. Japan Acad.*, **27**, 415 (1951); H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, **73**, 876 (1951).
(7) T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Japan Acad.*, **27**, 419 (1951).
(8) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama, Ibid., **26**, 38 (1950).
(9) T. Nozoe, S. Seto, H. Takeda, S.Morosawa, and K. Matsumoto, Ibid., **27**, 556 (1951).
(10) T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, Ibid., **27**, 18 (1951).
(11) T. Nozoe, T. Mukai, and K. Matsui, Ibid., **27**, 646 (1951).
(12) T. Mukai, M. Kunori, H. Kishi, T. Muroi, and K. Matsui, Ibid., **27**, 410 (1951).
(13) T. Nozoe, *Science of Drugs*, **3**, 174 (1949); *Sci. Rep. Tohoku Univ.*, **34**, 199 (1950).
(14) T. Nozoe, Y. Kitahara, and K. Doi, *Proc. Japan Acad.*, **27**, 156 (1951).
(15) T. Nozoe, Y. Kitahara, and K. Doi, *J. Am. Chem. Soc.* **73**, 1895 (1951).
(16) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**, 876 (1951).
(17) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941); Cf. also M. Kasha, Discussions of the Faraday Society, 1950, p. 14.

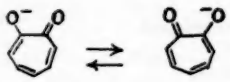
appear: one due to the $N \rightarrow V_n$ type transitions and the other due to the $N \rightarrow E_n$ type transitions. The bands of the first kind are related to the π-electrons extending along the entire system of conjugated bonds and are strong in intensity ($\varepsilon \fallingdotseq 10^4$); while the bands of the second kind are related to the electrons in the non-bonding molecular orbital, largely localized on the oxygen atom and are weak in intensity ($\varepsilon \fallingdotseq 10^3$). All the observed bands of the compounds now at issue are strong in intensity ($\varepsilon \fallingdotseq 10^4$), and hence may be assigned to the transitions of the $N \rightarrow V_n$ type, but not to the transitions of the $N \rightarrow E_n$ type.

The two bands in the 300—400 mμ and 200—300 mμ regions in the spectra of type A may be regarded as due respectively to $N \rightarrow V_1$ and to $N \rightarrow V_2$ transitions in a seven-sided ring system composed of conjugated three C=C's and one C=O, viz. a system composed of the field; and eight π-electrons. Octatrienal, which has also conjugated three C=C's and one C=O, shows a band at 306 mμ, and this was explained by McMurry[17] as due to the $N \rightarrow V_1$ transition. The 300 mμ band in the spectra of type A may be of the same nature as this 306 mμ band.

Tropolone anion may be regarded as a system composed of a field; and ten π-electrons. According to Dewar's molecular orbital treatment,[18] the two bands in the 300—400 mμ region as well as the bands in the 200—300 mμ region may be explained as due to the $N \rightarrow V_n$ transitions in the system just mentioned. The fact that tropolone and its derivatives exhibit spectra of type B, as tropolone anion, may be taken as indicating that they bear a closer resemblance in the electronic state to tropolone anion than to tropolone methyl ether and tropolone acetate, which exhibit spectra of type A. This may in turn indicate that there is a resonance in tropolone somewhat similar,



which resembles the resonance in tropolone anion,



The resonance as above cannot occur in tropolone methyl ether and tropolone acetate, there being no intramolecular hydrogen bond in these compounds. The spectrum of aminotropone (Fig. 10) belongs also to the "Anion type" (type B), indicating that its electronic state resembles that of tropolone anion. The intramolecular N-H...O bonding in this compound seems to act like the O-H...O bonding in tropolone.

II. Effect of Substitution on the Positions of the Bands.—Though, as has been stated above, various spectra belonging to both type A and type B resemble one another in their general feature, they differ from ons another in the positions of their corresponding bands. Of the spectra of type A, that of tropone shows the bands at the shortest wave-lengths, and when Br, isoC_3H_7, OCH_3, or $OCOCH_3$ are substituted for the hydrogen atoms of tropone, they shift toward longer wave-lengths. Of the pectra of type B, that of tropolone shows thee bands at the shortest wave-lengths, and the substitution of Br, CH_3, etc. for the hydrogen atoms of tropolone also causes the shifting of the bands toward longer wave-lengths.[19] The amounts of these shifts ($\Delta\nu$) are shown in Table 2. As may be seen from the table, the shift of the bands is greatest when the substituent is NH_2, and it becomes less in the order of OH, Br, and alkyl radicals. This order of the amount of shift for different substituent radicals is reverse to the order of the ionization potentials of the radicals.[20] There is a tendency that *p* (or 5)-substitution of tropolone (Figs. 12 and 17) gives in general a larger red-shift than *m* (or 4)- or *o* (or 3)-substitution (Figs. 11, 15, and 16); and the amount of the red-shift is approximately additive when two or more radicals are substituted for the hydrogen atoms in one tropolone ring.

These shifts of the bands caused by substitution may be explained as due to the electron migration from the substituent radicals toward the seven-membered ring of the tropone. K. F. Herzfeld[21] advanced a general theory on the electron migration from the substituent radicals toward the conjugated double-bond

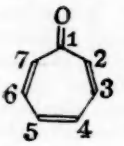
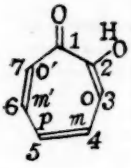
(18) M. J. S. Dewar, *Nature*, **166**, 790 (1950).

(19) *O* (or 3)-and *m* (or 4)-alkyl substitut'ons are exceptional; they cause a little shifting of the bands toward shorter wave-lengths.

(20) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(21) K. F. Herzfeld, *Chem. Rec.*, **41**, 233 (1947).

Table 2

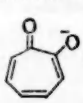
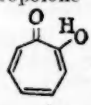
Fundamental System	Substituents	Positions of Absorption Peaks of the Longest Wave-Lengths		Shiftings due to the Substitution ($\Delta\nu$), cm^{-1}
		$m\mu$	cm^{-1}	
	Nothing	310	32200	—
	2-$OCOCH_3$	317	31500	−700
	2-OCH_3	321	31100	−1100
	2-OCH_3-4-$isoC_3H_7$	325	30700	−1500
	2,4,7-Br_3	349	28600	−3600
	Nothing	374	26700	—
	o(or 3)-CH_3	372	26800	+100[19]
	m(or 4)-CH_3	372	26800	+100[19]
	p(or 5)-CH_3	379	26400	−300
	m(or 4)-$isoC_3H_7$	372	26800	+100[19]
	o(or 3)-Br	385	25900	−800
	p(or 5)-Br	389	25700	−1000
	o, *p*(or 3,5)-Br_2	392	25500	−1200
	o, *p*, *o'*(or 3,5,7)-Br_3	407	24500	−2200
	m(or 4)-$isoC_3H_7$-*o'*(or 7)-OH	379	26400	−300
	m(or 4)-$isoC_3H_7$-*o'*(or 7)-NH_2	402	24800	−1900

system, and H. Baba and S. Nagakura[22] made a correction and a supplement to it. According to this theory, the lower the ionization potential of the substituent is, the greater must be the extent of the migration, and accordingly the greater must be the shift of the band caused by the migration; and when the substituent radicals are more than one, the amount of the shift must be the sum of the shifts caused by respective radicals. All these consequences of the theory are in good agreement with what has been observed of the shifts of the bands due to substitutions in tropone and tropolone.

The Baba-Nagakura theory claims that the band due to N→E_n transition should shift on substitution toward shorter wave-lengths. Then, the fact that all the bands of tropone and tropolone that have been treated in this paper shift on substitution toward longer wave-lengths must be, according to the theory, an indication that these bands are not due to N→E_n transitions. This is what has already been concluded from the intensity measurements of these bands (page 372).

III. Miscellanies.—Some interesting facts which have come to the writer's notice in the course of the present work are recorded below:

(1) The spectrum of 2-phenyltropone as well as that of 2-phenyl-4 (or 6)-isopropyltropone corresponds nearly to the superposition of the spectra of tropone and benzene. This fact shows that there is but little interaction between π-electrons of the seven-membered ring and the benzene ring in 2-phenyltropone or 2-phenyl-4 (or 6)-isopropyl-tropone.

(2) The spectrum of tropolone in neutral water corresponds exactly to the superposition in a certain proportion of the spectra of tropolone in NaOH (Fig. 7) and of tropolone in HCl (Fig. 9). This fact shows that in the aqueous solution of tropolone two forms of molecules  and  coexist.

(3) The absorption bands of tropolone acetate (Fig. 1) are situated at slightly shorter wave-lengths than those of tropolone methyl ether (Fig. 2). An explanation of this fact may be that the nonbonding electrons on the oxygen atom attached to the 2-carbon atom (C_2) in tropolone acetate migrate partly toward the acetyl group and partly toward the seven-membered ring, while those of tropolone methyl ether migrate exclusively toward the seven-membered ring.

(4) The vibrational structures of the spectra of *o*-, *m*-, and *p*-methyl tropolones are considerably different from one another (Figs. 15, 16, and 17), while they bear a striking resemblance respectively to those of *o*-, *m*-, and *p*-isopropyl tropolones (α, β, and γ-thujaplicins).[23] Similarly the vibrational structures of the spectra of *o*- and *p*-methyl tropolones

(22) H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, **72**, 72, 74 (1951).

(23) A. Aulin-Erdtman, *Acta. Chem. Scand.*, **4**, 1031 (1950).

resemble respectively to those of *o*-, and *p*-bromotropolones (Figs. 11 and 12). In general, the features of the vibrational structures in the spectra of the tropolone ring appear to be determined by the positions, rather than the kinds, of the substituent radicals.

(5) Of *o'*-hydroxyhinokitiol (Fig. 19), three isomers, α(m. p. 60°C.), β(m. p. 52°C.), and γ(m. p. 46°C.) have been obtained by T. Nozoe et al.[14] The spectra of these three isomers are exactly alike in the positions of all the absorption peaks, but differ from one another in the absorption intensities of the bands. According to the present writer's near infra-red absorption studies, there is evidence which indicates that these three isomers differ from one another in the state of their intramolecular hydrogen bonds.

The writer wishes to express his sincere thanks to Professors San-ichiro Mizushima, Takehiko Shimanouchi, and Saburo Nagakura of Tokyo University for their kind guidance in this work, and to professor Tetsuo Nozoe, Messrs. Shuichi Seto, Yoshio Kitahara, Toshio Mukai, and their co-workers in Tohoku University for placing the samples at the writer's disposal and for their valuable advice.

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Mechanical Properties of Concentrated Hydrogels of Agar-agar. I. Modulus of Elasticity in Compression

By Hiroshi FUJITA, Kazuhiko NINOMIYA and Terutake HOMMA

(Received January 31, 1952)

Introduction

The variation in mechanical properties of gels of high-polymeric substances is perhaps one of the most interesting problems of research in the field of rheology. Recent advances in rheology have resulted in the development of theories which permit interpretation of various mechanical properties of high polymers in terms of molecular quantities. However, papers dealing with the mechanical properties of polymer gels from the rheological point of view are still few in the literature. Remarkable progress has recently been made by Ferry[1] and his coworkers for the mechanical behavior in a variety of protein gels such as gelatin and fibrinogen gels. The experimental data accumulated in their studies have since been almost all concerned with the elasticity of the materials investigated, and few data have yet been obtained for the viscoelastic behavior of the materials.

Various aspects of physico-chemical properties of agar-agar gels have been reported, but there is little information available on their mechanical properties. For this reason, Nakagawa et al.[2-5] have set up a series of experimental studies on the rheological properties of hydrogels of agar-agar, and have published several interesting papers which are chiefly concerned with the elastic behavior at very low concentrations. In order to complete our understanding of the mechanical behavior of hydrogels of agar-agar, it is also of considerable interest to extend their research to a region of higher concentrations than they treated.

In this paper, the results of a study of the elastic behavior in compression of agar-agar hydrogels at concentrations between 2g./100 cc. and 4 g./100 cc. are reported.

Material and Apparatus

The material used was a grade of powdered agar-agar, from which the test pieces of agar-agar hydrogels were made according to the procedure which will be described below. No fractionation of the sample was made. It is well realized that the physico-chemical properties of any gel-system are appreciably influenced by the

(1) See, for example, J. D. Ferry, "Advances in Protein Chemistry," IV, Academic Press Inc., Publishers, New York, 1948, p. 1-78.

(2) T. Nakagawa, *Kagaku*, **20**, 130 (1950).
(3) T. Nakagawa, *J. Chem. Soc. Japan*, **72**, 390 (1951).
(4) T. Nakagawa and T. Danno, *J. Chem. Soc. Japan*, **72**, 518 (1951).
(5) T. Danno, *J. Chem. Soc. Japan*, **72**, 1061 (1951).

conditions under which the gel to be studied was formed. Accordingly, in order to produce experimental data which will ultimately be suited for quantitative discussions, it is necessary to take a consistent process in the course of preparing the sample gels. In this investigation the following procedure was employed consistently.

A mixture of the agar-agar powder and distilled water which was prepared to a desired concentration was boiled for 30 min. to make it sol. The sol was transferred into a glass cylinder, whose height and inner diameter were both about 3 cm., and chilled for 1 hr. in rest air kept at 25°C. to make it hard. Picking out the gel thus formed from the cylinder, a rod-shaped test specimen was obtained; over the concentration range as was treated in this work (2 g./100 cc.~4 g./100 cc.), all the specimens were rigid enough to support their own weight, or to be amenable to measurements by means of an apparatus which will be described below. The specimen was then quickly inserted in the apparatus and stood there for 30 min. The apparatus was installed in an air thermostat which had been previously controlled to a desired temperature. Some preliminary observations indicated that the test piece, as a whole, reached a temperature almost equal to that in the thermostat when it was placed there for about 30 min. In the case of as low temperature as 5° to 10°C., a somewhat longer time was required before arriving at the thermal equilibrium. For these reasons, except in the case of investigating the effect of gelation time, all the measurements were taken after 30 min. from the introduction of the specimen into the apparatus.

The apparatus used in this experiment was a modified form of the chainomatic balance used by Dart and Guth[6] for the study of the mechanical properties of natural cork. A schematic diagram of the apparatus is shown in Figure 1. Differing from Dart and Guth's original apparatus where desired compression stress-strain curves had to be determined manually, the present apparatus was designed so that a continuous smooth locus corresponding to a compression stress-strain curve could be recorded automatically on a chart paper mounted on the rotating cylinder. Because of the limit of space, accounts of the mechanical principle of the apparatus as well as the method of measurement must be omitted here; detailed descriptions of them will be made in a separate paper.[7]

Temperatures inside the thermostat (from about 5° to 60°C.) were controlled to about ±0.25°C. over the entire operating range in a particular run. Humidity was maintained at an almost saturated state to prevent drying of the specimen gel as much as possible.

The bundle of chains in the apparatus was

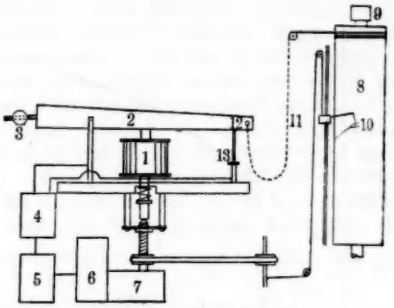

Fig. 1.—Experimental apparatus; 1: sample. 2: balance arm. 3: balast. 4: relay. 5: battery. 6: motor. 7: gear box. 8: chart cylinder. 9: driving clock. 10: pen. 11: chains. 12: hanger. 13: contact point.

lowered at a constant rate of falling with rotation of the chart cylinder at a constant speed. Accordingly, all the stress-strain curves obtained in this experiment should be accepted as the stress-strain curve for a constant rate of loading, or approximately, for a constant rate of increase in stress. The rate used herein was about 1000 dynes/cm.²/sec. In converting the locus recorded on the chart cylinder to the corresponding stress-strain curve it was necessary to know the value of Poisson's ratio for the sample. In this study, it was simply presumed to be 0.5 without making any experimental determination for it.

Results and Discussion

Typical compression stress-strain curves obtained at various conditions are shown in Figures 2 and 3, where γ denotes the strain and S the stress. All the stress-strain curves obtained invariably have a general tendency similar to that found in the curves in the

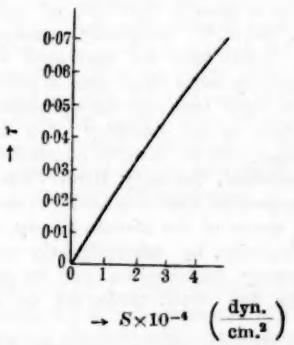

Fig. 2.—Stress-strain curve for a sample of 3 g./100 cc. conc. at 25°C. after 90 min. chilling.

(6) S. L. Dart and E. Guth, *J. Appl. Phys.*, **17**, 314 (1946); ibid., **18**, 476 (1947). See, also, R. S. Witte and R. L. Anthony, *J. Appl. Phys.*, **22**, 689 (1951).

(7) K. Ninomiya, *J. Chem. Soc. Japan*, in preparation.

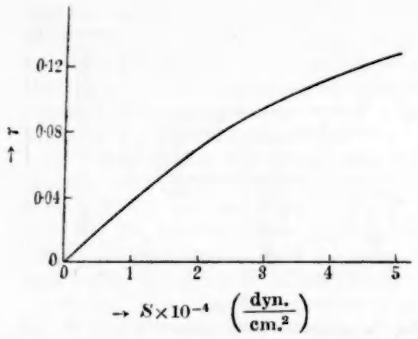

Fig. 3.—Stress-strain curve for a sample of 2 g./100 cc. at 23°C. after 90 min. chilling.

figures; for moderately small values of stress the strain increases linearly with the stress, while at higher stresses the plot is gradually curved toward the stress-axis, thus revealing a certain non-linearity. Relative length of the portion where Hooke's law holds very closely was found to be largely affected by experimental conditions. Some hysteresis loop was observed in the stress-strain curve when a cyclic process of loading was applied to the specimen. Since, however, it was almost negligible within the limits of deformations tested, it was presumed that all test pieces used in this work would be purely elastic for at least sufficiently small strains. The modulus of elasticity (Young's), E, was evaluated using the slope of the linear part in the stress-strain curve, and it was found that, in the range of test conditions herein adopted, the value of E fell in a range of about 10^5 dynes/cm.^{2}~10^6 dynes/cm.^{2}; for example, E for an agar-agar hydrogel of concentration 4 g./100 cc. was about 10^6 dynes/cm.^{2} at temperature 25°C. This value is, in effect, almost comparable to the value of E for a gelatin hydrogel of concentration 18.6 g./100 cc.[8] Generally speaking, it may be concluded that an agar-agar hydrogel is considerably more rigid than a gelatin gel.

There have been various opinions regarding the origin of the elasticity of a hydrogel of agar-agar, but no definite conclusion has yet been attained. Recently, Hirai[9] has attempted to interpret the elastic behavior of an agar-agar gel in terms of the kinetic theory of rubber-like elasticity, by taking partly into account the energy contribution due to interactions between the chain molecules of agar-agar. Although he has reached a result which is apparently in accordance with the experimental results on the relation between the modulus of elasticity and the temperature, there seem to be some ambiguous points in his development concerning the consideration of the energy contribution.

Dependence of the Modulus of Elasticity upon Concentration.—This is a primarily interesting problem in the study of mechanical properties of a gel-system. Experiments were performed at 25°C. by varying the concentration from 2 g./100 cc. to 4 g./100 cc. The results obtained are plotted in Figure 4, where C is the concentration in percentages. From this figure the data prove to fit the following simple relation:

$$E=k \cdot C^{1.7}, \qquad (1)$$

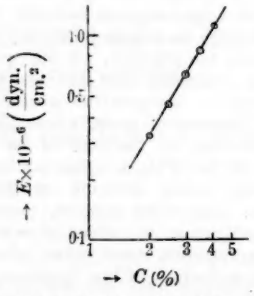

Fig. 4.—Concentration dependence of the modulus of elasticity, E, at 25°C. after 90 mim. chilling.

where k is a proportionality constant. With hydrogels of gelatin, it was frequently reported by many workers[10~12] that the relation:

$$E=k \cdot C^2 \qquad (2)$$

well described the data, though in some cases the exponent in Eq. (2) had to be taken as slightly less than 2. With fibrin clots (gel of fibrinogen containing small amount of thrombin), Ferry and Morrison[13] provided the relation:

$$E=k \cdot C^{1.57}. \qquad (3)$$

Ferry[11] also showed for hydrogels of gelatin that the exponent 2 in Eq. (2) was hardly affected by change in temperature.

(8) R. Houwink, "Elasticity, Plasticity and Structure of Matter" Cambridge University Press, London, 1937, p. 275.

(9) N. Hirai, *J. Chem. Soc. Japan*, **73**, 65 (1952).

(10) S. E. Sheppard and S. S. Sweet, *J. Am. Chem. Soc.*, **43**, 539 (1921).

(11) J. D. Ferry, *J. Am. Chem. Soc.*, **70**, 2244 (1948); See, also, reference (1).

(12) N. Hirai, *J. Chem. Soc. Japan*, **72**, 837 (1951).

(13) J. D. Ferry and P. R. Morrison, *J. Am. Chem. Soc.*, **69**, 388 (1947); See, also, reference (1).

Dependence of the Modulus of Elasticity upon Temperature.—Keeping the agar-agar concentration at 4 g./100 cc., measurements were made at several temperatures between 5° and 63°C., and the plot indicated in Figure 5 was obtained, where θ is the temperature in centigrades. This plot is seen to have a similar appearance to that obtained by Ferry et al.[14][11] for gelatin hydrogels and, also, to that by Nakagawa et al.[4][5] for agar-agar hydrogels of very low concentrations. At higher temperatures than about 60°C. the test pieces used became less rigid even at a concentration as high as 4 g./100 cc. The apparatus used in this work, however, was safely applicable only to the specimen rigid enough. Accordingly, the data given above would necessarily be somewhat incorrect in such an elevated temperature region. Hysteresis of the modulus in a cyclic temperature change was not studied in this work.

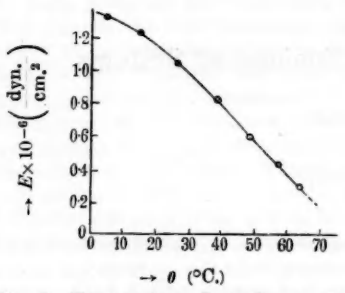

Fig. 5.—Temperature dependence of the modulus of elasticity, E, at 4 g./100 cc. after 90 min. chilling.

Effect of Gelation Time upon the Modulus of Elasticity.—For hydrogels of gelatin and fibrin clots, the effect of gelation time upon their rigidity was investigated in detail by Ferry et al.,[11][13][1] but for agar-agar gels there is no information on this problem. In view of this, the following experiment was conducted.

A number of glass cylinders filled with a hydrosol of agar-agar of known concentration were inserted simultaneously in the thermostat kept at 25°C. and allowed to stand there for an appropriate time (from 40 to 60 min.) to make the sol hard. The specimen gels were then successively subjected to measurements one by one at a suitable interval of time. The measurement was extended over an interval of about 170 min. for each concentration. Thus, the results plotted in Figure 6 were obtained, where t_g is the gelation time in minutes, being defined as the time which has elapsed after the cylinders were introduced in the cooling chamber. It is seen that within the first several ten minutes there was a fairly rapid increase of the modulus of elasticity but this increase was followed by a very gradual approach to a constant value. The higher the concentration, the more rapid the initial development of E resulted. It is worthy of notice here that the plotted curves indicate that the 90 min. chilling procedure as used in all other measurements than those described in this section was almost enough to assure the steady state values of E. Similar plots as shown in Figure 6 were already obtained by Ferry et al.[11][13] for both gelatin hydrogels and fibrin clots; for gelatin hydrogels the plot did not approach a final state even after more than 10 hr. had elapsed for all the cases investigated, while for fibrin clots it required only about 1 hr. before attaining a steady state. The latter result may be compared with our result for hydrogels of agar-agar.

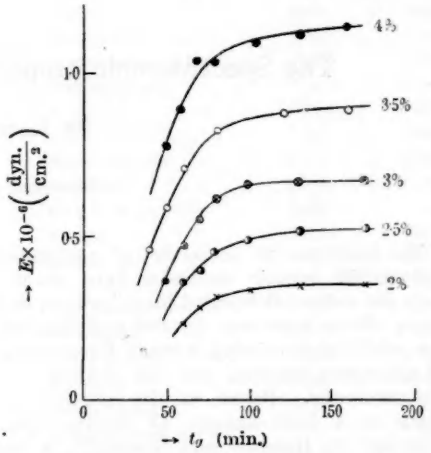

Fig. 6.—Effect of gelation time, t_g, on the modulus of elasticity, E, at various concentrations.

Summary

As the first step in a series of works on the mechanical behavior of a concentrated hydrogel of agar-agar, the experimental determination of its elastic behavior in compression was made. An apparatus which could record a compression stress-strain curve automatically

(14) J. D. Ferry and J. E. Eldridge, *J. Phys. & Colloid Chem.*, **53**, 184 (1949).

was devised and used to obtain the results reported in this paper. Influences of temperature, concentration, and gelation time upon the modulus of elasticity (Young's) were considered and plotted in Figures 4, 5 and 6.

The authors wish to thank Mr. T. Nakagawa of the University of Tokyo for helpful advice and encouragement given in the course of this study. Thanks are also due to Mr. T. Maki of this laboratory for his assistance in measurements.

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The Spectroscopic properties of Conjugated Systems

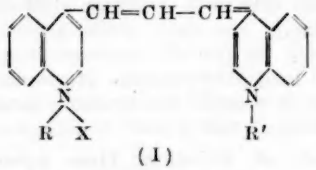
By Kazuo SHIBATA

(Received April 11, 1952)

The spectroscopic properties of conjugated systems in organic molecules have already been the subject of repeated investigations, and many efforts have been devoted to finding out the relationship existing between the positions of absorption maxima and the structures of the molecules. Based on the observations made on a large number of cyanine dyes, especially by Hamer[1] and Brooker[2], it has been stated that there exists an approximately linear relationship between the wave length of the absorption maximum and the length of conjugated system, whereas Kuhn and Hausser[3] showed that in the case of other types of conjugated systems such as diphenyl polyenes, the square of the wavelength of absorption maximum is related linearly to the length of conjugated systems.

These relationships, especially the one found for cyanine dyes were interpreted by Lewis and Calvin[4] semi-classically and later by Sklar and Herzfeld[5] and Bayliss[6] quantum mechanically. It should, however, be noticed that the linear relationships in question are not only the approximate ones, but also that there have been found a number of cases that are apparently at variance with them. In order to obtain a coherent understanding of the electronic states of conjugated systems, it is desirable to scrutinize more in detail and more systematically the spectroscopic properties of conjugated systems with a large variety of chemical compounds. From this point of view the present work was devoted to investigations of the spectroscopic properties of a large number of cyanine dyes and styryl dyes as well as polyene type compounds.*

(1) The Effect of Substitutions and the Solvents upon the Position of Absorption Maximum.—Preliminary observations were



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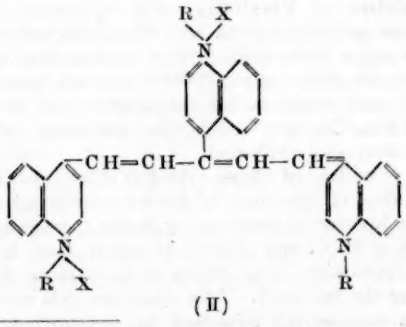


(II)

(1) Hamer, *J. Chem. Soc.* 125, 1348 (1924); **1930**, 903 **1936**, 1225; **1932**, 251; **1928**, 206.
(2) Brooker, *J. Am. Chem. Soc.* **57**, 2480, 2488, 2492 (1935); **58**, 659, 662 (1936); **59**, 67, 74 (1937).
(3) Hausser and Kuhn, *Z. Physik. Chem.*, B, **29**, 371, 378, 384, 391, 417 (1935).
(4) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Branch and Calvin, "The Theory of Organic Chemistry", 1941, p. 155.
(5) Herzfeld and Sklar, *J. Chem. Phys.* **10**, 508, 521 (1942).
(6) Bayliss, *J. Chem. Phys.* **16**, 287 (1948).

* The observations were made by photoelectric measurements, the accuracy of which was about ± 10 A.

The styryl and cyanine dyes used in this work were synthesized in the laboratories of Prof. E. Ochiai and of Dr. T. Ogata, to whom the writer wishes to express his hearty thanks for their kindness in placing the materials at the author's disposal.

made with various derivatives of cryptocyanine (I) and neocyanine (II), using water as the solvent.

As a rule, these cyanine compounds display two absorption bands in the visible region, the one at longer wave length being always stronger than the other. In some cases the existence of the weaker band is more or less obscured by the other. In the following, these two bands are referred to as the "first" (stronger) and the "second" absorption band. To begin with, we shall restrict our consideration only to the first absorption band. The results of our observations are summarized in Table 1 and 2, where λ_1 (in A.) means the wave length of the maximum of the first absorption band. From these data it may be seen that in so far as it concerns alkyl groups, the substitution of R and R′ does not cause any profound difference in λ_1, the maximum difference observed being only a few mμ. Nor does the substitution of the halogen X cause any significant shift of λ_1. Quite the same was true when, instead of water, ethanol was used as the solvent, for which the comprehensive data will be given in the latter part of this paper.

Table 1

Absorption Maxima of Cryptocyanines

R	R′	X	λ_1 in A.
$-CH_3$	—R	—I	6940
$-C_2H_5$	—R	:	6960
:	$-isoC_5H_{11}$	:	6960
:	$-CH_2-CH_2$ —OAc	:	6950
$-CH_2-CH_2-\phi$	—R	:	7320
$-CH_2-CO-NH_2$	—R	:	7220
$-CH_2-COOC_2H_5$	—R	—Cl	6960

Table 2

Absorption Maxima of Neocyanines

R	X	λ_1 in A.
$-CH_3$	—I	7560
$-C_2H_5$	:	7590
$-nC_3H_7$	:	7570
$-isoC_3H_7$	:	7540
$-nC_4H_9$	:	7590
$-isoC_4H_9$	:	7560
$-nC_5H_{11}$	:	7590
$-isoC_5H_{11}$	:	7550
$-CH_2-CH_2-OAc$	:	7580
$-CH_2-CH_2-\phi$	:	7620
$-CH_2-CH_2-O-CH_2-\phi$	:	7610
$-C_2H_5$	:	7590
:	—Cl	7520
:	—SCN	7520
:	$-NO_2$	7520
:	$-NO_3$	7530
:	$-SO_3-OC_2H_5$	7520
:	$-SO_3-\phi CH_3$	7510

Table 3

The Absorption Maxima of (I) and (II) observed in Various Solvents

Solvents	(I)	(II)
Water	6960	7610
Acetnitrile	7020	—
Acetic anhydride	7040	7720
Acetaldehyde	7045	—
Methanol	7050	7720
Ethyl acetate	7055	7750
Nitromethane	7055	7750
Acetone	7060	7730
Ethylene glycol	7085	—
Ethanol	7090	7760
Formamide	7090	7800
Chloroform	—	7830
Acetyl acetone	7100	—
Isobutanol	7110	—
Amyl acetate	7115	—
Pyridine	7155	8100
Benzyl alcohol	7185	—
Tetra-chloroethylene	7190	7730
Aniline	7205	—
Nitrobenzene	7235	7990

Using the compounds having ethyl group as R and R′ and iodine as X, the effect of solvents upon the value of λ_1 was investigated. The results obtained are summarized in Table 3. From this table it is apparent that λ_1 has the smallest value when water is used as solvent. It should be noticed that the absorption spectra observed in that case were markedly different from those observed in other organic solvents. Moreover, for reasons not yet clear, the light absorption in that case did not obey Beer's law which was found to hold satisfactorily true when ethanol or acetone were used as the solvent. Significant is the fact that ethanol gave the values of λ_1 which coincided within the limit of only ± 40 A. with those observed with the following solvents;

Acetic anhydride, Acetaldehyde, Methanol, Ethyl acetate, Nitromethane, Acetone, Ethylene glycol, Formamide and Chloroform.

Based on these findings, the measurements of λ in our further experiments were carried out, using exclusively ethanol as the solvent. In the discussions to be made later, reference will also be made to a number of data reported by other workers, especially those by Brooker[2]

and Hamer.[1] All data to be referred to are those obtained by using either ethanol or methanol as the solvent.

(2) The Relationship between λ^2 and the Number of Bonds in the Conjugated Systems of Various Symmetric Cyanine Dyes. — For various kinds of symmetric cyanine dyes, we made the plot of the square of λ_1 against the number of bonds in the conjugated systems, after the precedent of Lewis and Calvin[4] for the polyene type compounds. In this plot, only those substances having alkyl groups as R or R′ were taken into consideration, and taking into account the fact established in our preliminary experiments, the differences in those alkyl groups as well as in the halogen X were disregarded.

For a series of substances having the same terminal nuclei, a curve bending concavely towards the λ_1^2-axis was obtained, and for another series of symmetric cyanine dyes with different kinds of terminal nuclei, another curve bending also in the same way was obtained. These curves do not generally coincide, but run almost exactly parallel to each other. This is schematically illustrated in Fig. 1, where n′ means the number of bonds between the two terminal nuclei and the curves CGD and EHF are those obtained for

$$A-(CH=CH)_l-CH=A \qquad (III)$$

and

$$B-(CH=CH)_l-CH=B \qquad (IV)$$

respectively. For this rule we shall adduce a large number of concrete examples in later paragraphs. Interesting is the fact that the similar relation also holds for the second absorption band, as will be discussed later.

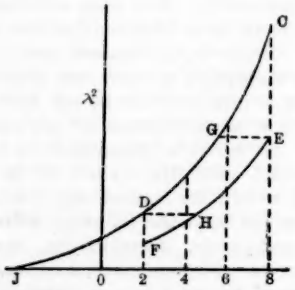


Fig. 1.

(3) The Concept of the "Color Factor" and its Characteristics.—The fact that the curves mentioned above run parallel to each other indicates that the lateral position of each curve is determined by the nature of the terminal nuclei. Let us assume a corresponding curve starting from the origin of the coordinate. Referring to this standard curve, the length JO may be regarded as due to the effect of the two nuclei of A.

In the following this value will be called the "color factor" of the nuclei of A. Color factors found experimentally for various kinds of nuclei are listed in Table 4. About half of the data given in the table are those obtained for polyene type compounds, which will be considered in later discussions.

Of great interest is the fact that in some cases there exists an additivity relation in the values of color factors. The difference between the color factor for a nucleus and that of the corresponding benzo-nucleus was found to be always 0.3. Therefore, the color factor of benzothiazole, for example, can be calculated by adding 0.3 to the color factor of thiazole (1.80).

Extending the concept of the color factor to the whole molecule of a compound, its value can be computed by adding the color factors of nuclei in the molecule and the number of bonds in the conjugated system. For example, the color factor of cryptocyanine is 11.10, because the color factor of quinoline linked at the position 4 is 3.55, and the number of bonds connecting the two quinoline nuclei is 4. We shall designate the color factor of a molecule by n in later discussions.

(4) Empirical Formula for the Standard λ^2-n-curve. — The significance of the color factor of each compound lies in the fact that it enables us to calculate the value of λ_1 with appreciable accuracy. It was found that the following equations fit in well with the standard curves for λ_1 (in $10^3\times$A. unit).

$$\lambda_1^2=n/(0.36-0.0123\,n) \qquad (1)$$

The curve C_1 in Fig. 2 is drawn according to Eq. (1) by plotting the square of the observed values of λ_1 against n, which in turn was calculated from the values given in Table 4.

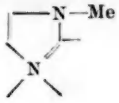
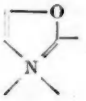
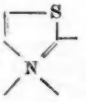
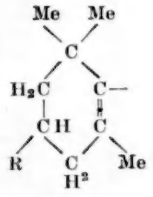
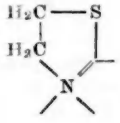
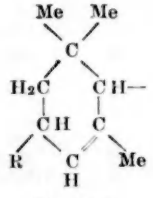
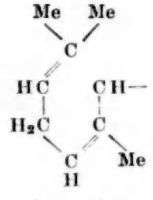
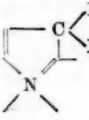
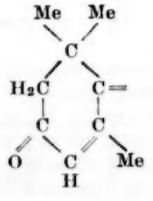
By plotting the square of the observed values of λ_2 against the same values of n, as was done for the first absorption bands, we obtain the standard curve for λ_2. In this case, Eq. (2) of the same form fits in fairly well.

$$\lambda_2^2=n/(0.40-0.0124\,n) \qquad (2)$$

The curve C_2 in Fig. 2 is drawn according to this equation.

Table 4

The Values of "Color Factors" for Various Nuclei

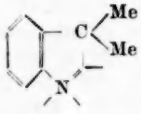
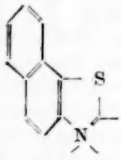
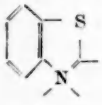
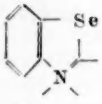
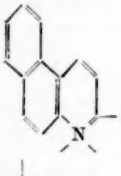
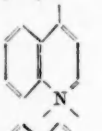
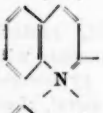
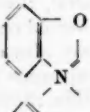
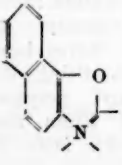
CH—CH=CH	2.00		0.98	C=O	2.00
	0.98		2.30		4.0
	1.80		3.25		2.0
	0.85		2.35		1.5
	1.85		+0.30		3.5
	1.63		3.00		5.0

For some important symmetric and asymmetric cyanine dyes, the calculated and observed values of λ_1 are compared in Tables 5 and 6. As may be seen from these tables, the agreement between the two values is satisfactory for symmetric dyes, while the values calculated for asymmetric dyes are always somewhat lower than the observed ones. The reason of this disagreement will be discussed later.

(5) **Analogous Relation Existing for Polyene and some other Compounds.**—It may be highly interesting to note that what we have established for cyanine type compounds was also found to hold, mutatis mutandis, for other types of compounds with conjugated systems. The polyene type compounds are known to have, in general, three absorption bands, among which the second one is the strongest and the other two have almost the same intensity. For these compounds a close examination of the λ^2-n'-relation shows that it is non-linear; contrary to the case of cyanine dyes, the curves bend concavely toward the n′-axis. Using the spectroscopic data for diphenyl polyenes ϕ—$(CH=CH)_l$—ϕ reported by Kuhn and Hausser[3], and assuming the color factor of

Table 5

The Symmetric Cyanine Dyes
A—(CH=CH)$_l$—CH=A

A	l	$\lambda_{cal.}$	$\lambda_{obs.}$
	1	5460	5450
	2	6420	6360
	3	7430	7450
	0	4980	4550
	1	5930	5950
	2	6910	6890
	3	7970	7990
	0	4650	4220
	1	5590	5570
	2	6570	6500
	3	7590	7620
	0	4380	4380
	1	5670	5700
	2	6640	6600
	3	7670	7700
	0	5430	5530
	1	6400	6350
	2	7400	7380
	1	6290	6300
	0	6050	5910
	1	7040	7090
	2	8100	8100
	3	9290	9320
	0	5150	5220
	1	6100	6050
	2	7090	7080
	3	8160	8080
	0	3870	3720
	1	4840	4850
	2	5790	5800
	0	4170	3990
	1	5130	5140
	2	6070	6070

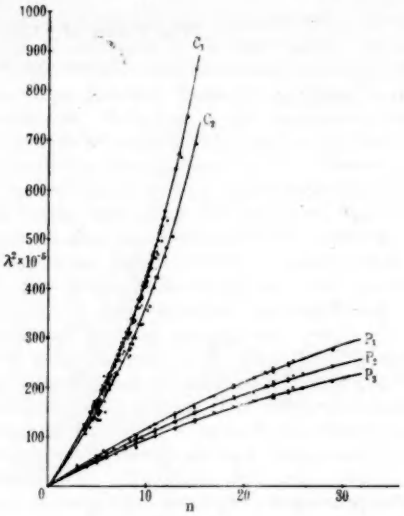
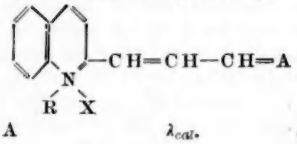
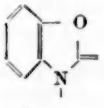
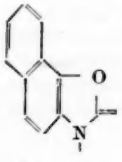
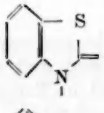
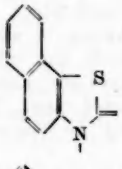
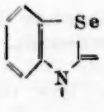


Fig. 2.

Table 6

The Asymmetric Cyanine Dyes



A	$\lambda_{cal.}$	$\lambda_{obs.}$
	5470	5450
	5610	5640
	5850	5600
	6020	5990
	5880	5820

the phenyl group to be 3, we obtain the following empirical formulas for the standard curves of the three bands, which are again of the same form as before;

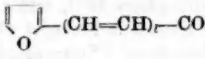
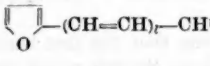
$$\lambda_1^2 = n/(0.80+0.008\,n) \quad (3)$$

$$\lambda_2^2 = n/(0.84+0.012\,n) \quad (4)$$

$$\lambda_3^2 = n/(0.92+0.015\,n) \quad (5)$$

Striking is the fact that these empirical formulas not only fit in well with diphenyl polyenes but also with the other compounds listed in Table 7 and with carotinoids (α- and β-carotene, lycopine, cryptoxanthine, crocetin etc.) if we assume the suitable values of the color factors given in the last column of Table 4. These assumed values of color factors are resonable from the consideration of the number of double bonds in the nucleus.

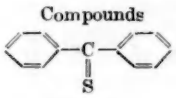
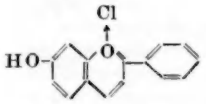
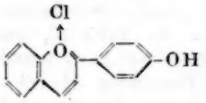
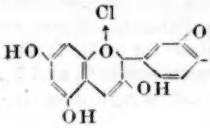
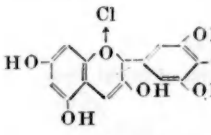
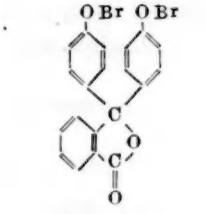
Table 7

Compounds	l
ϕ—(CH=CH)$_l$—ϕ	1—7
CH_3—(CH=CH)$_l$—CH_3	4—6
CH_3—(CH=CH)$_l$—CH_2—OH	1—4
ϕ—(CH=CH)$_l$—H	1—2
CH_3—(CH=CH)$_l$—COOH	1—3
CH_3—(CH=CH)$_l$—CHO	1—3
	0—3
	0—3

The curves P_1, P_2 and P_3 in Fig. 2 were drawn according to these equations and the points on these curves are those obtained by plotting the observed values of λ^2 against n, which were calculated from the values of color factors given in Table 4.

Besides cyanine and polyene compounds, there is another group of coloring substances which apparently, and in a peculiar manner, obey the above mentioned rule. The compounds listed in Table 8 have the property in common that they have two distinct absorption bands separated rather widely. If we plot the square of λ_2 (the absorption band at shorter wave length) on the standard line P_2 in Fig. 2, the point for the square of λ_1 was found to fall exactly upon curve C_1 against one and the same value of the color factor. For example, the points for λ_1 and λ_2 of thiobenzophenone fall on curves C_1 and P_2, respectively, with the color factor of 9.5. The same was true with all other compounds listed in Table 8, in which the color factors estimated in the above mentioned manner are also given for comparison.

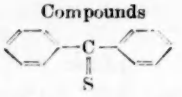
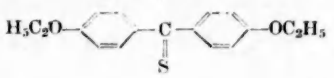
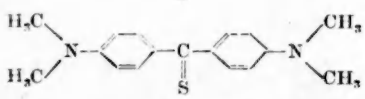
Table 8

Compounds	λ^2 (λ in $10^3\times$A. unit)		n
	9.9	38.4	9.5
	5.9	19.8	5.7
	6.3	21.2	6.0
	7.3	26.0	7.0
	7.6	27.6	7.2
	9.3	32.1	8.3

From the facts described above, it may be inferred that the compounds listed in Table 8 have both cyanine and polyene types of absorption bands. It should, however, be added that while unsubstituted thiobenzophenone follows our rule satisfactorily, the applicability of the rule is rather unsatisfactory in the case of some substituted thiobenzophenones. In Table 9 are shown the data reported by Burawoy[7]. For substituted thiobenzophenones we cannot find any definite value of color factor, on the basis of which the points for the two bands may be brought exactly upon the curves C_1 and P_2, respectively, in Fig. 2. If we assume for these substances the value of color factor which had been used for unsubstituted thiobenzophenone, the point for λ_1 falls lower than curve C_1 and the point for λ_2 falls above curve P_2.

(7) Burawoy; *J. Chem. Soc.*, **1939**, 1177.

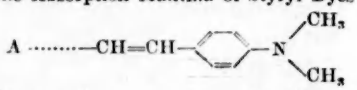
Table 9

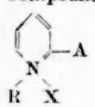
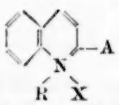
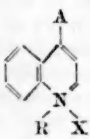
Compounds	λ^2 (λ in $10^3 \times$ A. unit)		Solvents
	9.9	38.4	hexane
	—	36.9	ether
	11.8	35.5	hexane
	12.5	33.5	ethanol
	—	32.8	hexane

The similar discrepancy from our rule was observed with styryl dyes. In Table 10, are given the values of λ which we have found for some styryl dyes. The value of color factors of these compounds can be calculated from the values given in Table 4. When we plot the square of λ against the color factor, the point for λ falls between curves C_1 and P_2. This was the case with all styryl dyes investigated.

Table 10

The Absorption Maxima of Styryl Dyes



Compounds	$\lambda_{obs.}$ in A. unit
	4670
	5270
	5460

As we have seen, our rule has proved to be quite satisfactory for certain groups of compounds, while it gives more or less deviating values for some other groups of compounds. In the following, an attempt will be made to elucidate the causes underlying the diversity of spectroscopic properties of different types of compounds.

(6) Interpretations of the Different λ^2-n-Relationships shown by Different Groups of Compounds.—In 1939 Burawoy[7], investigating the spectroscopic properties of various kinds of compounds, made the interesting observation that the two absorption bands shown by thiobenzophenones behave differently under certain conditions. On changing the solvent from a non-polar one to a polar one, it was found that the band at longer wave length was shifted towards shorter wave length, while the other band was displaced towards longer wave length (See Table 9). A similar phenomenon was observed when the dipole moment of the substance was enhanced by introducing some radical in it. These phenomena indicate that the structures in the molecules, which are responsible for the two bands are essentially different in nature. According to Burawoy, the band situated at longer wave length is caused by a chromophore of ionic nature ("chromophore R"), while the band at shorter wave length is brought about by a non-ionic chromophore ("chromophore K").

We have already seen that the first band of thiobenzophenone follows the rule of the bands of cyanine compounds, while its second band behaves exactly like the bands of polyene compounds. The data given in Table 3 show that the bands of cyanine compounds, like the band of thiobenzophenone at longer wave length, are shifted to violet by a change of the solvent which increases the dipole moment of the substances. Just the reverse phonomena are observed with polyene compounds; their bands, like the second absorption band of thiobenzophenone, are shifted to red with the increase of dipole moment by the effect of solvent. The same effect is brought about also by the substitution entailing an increase of dipole moment of polyene compounds.

It may safely be asserted that the polyene type compounds are non-ionic in any kind of solvent, while cyanine compounds will very likely assume ionic form in various solvents. At any rate, it may be certain that the Burawoy's chromophore R and K correspond to the conjugated double bond systems of cyanine and polyene compounds, respectively.

From this point of view, the compounds listed in Table 8 may be regarded as having the property of producing two types of molecule, ionic and non-ionic, in the solution.

(7) **Conclusion.**—By careful and detailed studies of a large number of absorption spectra of organic compounds with conjugated systems, we have found a rule governing quantitatively the relationship existing between the length of conjugated system and the absorption maximum. In alignment with these newly found λ^2-n-relationships, improvement of theoretical explanations such as Herzfeld and Sklar's is awaited with great interest.

As was remarked already, the rule we have found for symmetric cyanine dyes and polyene compounds does not apply with sufficient accuracy to some substituted thiobenzophenone and styryl dyes, nor for some asymmetric cyanine dyes. In these cases, our rule gives always higher values of λ for cyanine type absorption and lower values of λ for polyene type absorption. Systematic deviations in these cases indicate that in these compounds, besides the number of conjugated double bonds and the "color factor" of the terminal nuclei, some other factor plays a role in determining the position of the absorption band. The fact that our rule gives deviating values for substituted thiobenzophenone, while it applies satisfactorily to unsubstituted thiobenzophenone, suggests that the factor in question may be related to the dipole or the symmetry of the compounds. A theoretical explanation of this factor will be reported later in another work with more sufficient data on styryl dyes.

The author wishes to express his sincere thanks to Prof. E. Ochiai and Dr. T. Ogata for their kindness in placing the precious samples at the author's disposal.

The Tokugawa Institute for Biological Research, Tokyo

On Hydrogen Bonds Intimately Related with π-Electron Systems

By Masamichi TSUBOI

(Received May 29, 1952)

R. S. Rasmussen et al.[1],[2] pointed out that molecules such as, enolized β-diketones and salicyl aldehyde, which are characterized by the possession of both intramolecular hydrogen bond and C=O bond conjugated with other double bonds, show C=O vibration of abnormally low frequency. They suggested that in such molecules the hydrogen bond and the conjugated double bond system (or π-electron system) are intimately related to each other, and they called such molecules "conjugated chelate system". K. Kuratani, M. Tsuboi and T. Shimanouchi[3],[4] regarded that in tropolone (an isomer of salicyl aldehyde) the O—H···O bonding is intimately related to the seven-sided π-electron system. T. Shimanouchi and S. Mizushima[5] and M. G. Evans and J. Gergely[6] showed the possibility of electron transfer along the hydrogen-bonded long chain, ···HN—C=O···HN—C=O···, in proteins. This implies that the N—H···O bondings in it are intimately related to the π-electrons of C=O's. In general, in those molecules in which hydrogen bonds cooperate with π-electron systems to form a ring or a long chain, there are indications of a specially intimate relation between the hydrogen bonds and the π-electron systems.

The purpose of this paper is to present infrared and ultraviolet evidences which indicate that in these special molecules the hydrogen nuclei of the hydrogen-bonded OH

(1) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain. *J. Am. Chem. Soc.*, **71**, 1068 (1949).
(2) R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).
(3) K. Kuratani, M. Tsuboi and T. Shimanouchi, This Bulletin **25**, 250 (1952).
(4) M. Tsuboi, This Bulletin, **25**, 369 (1952).
(5) T. Shimanouchi and S. Mizushima, This Bulletin, **21**, 1 (1948).
(6) M. G. Evans and J. Gergely, *Biochemica et Biophysica Acta*. **3**, 188 (1949).

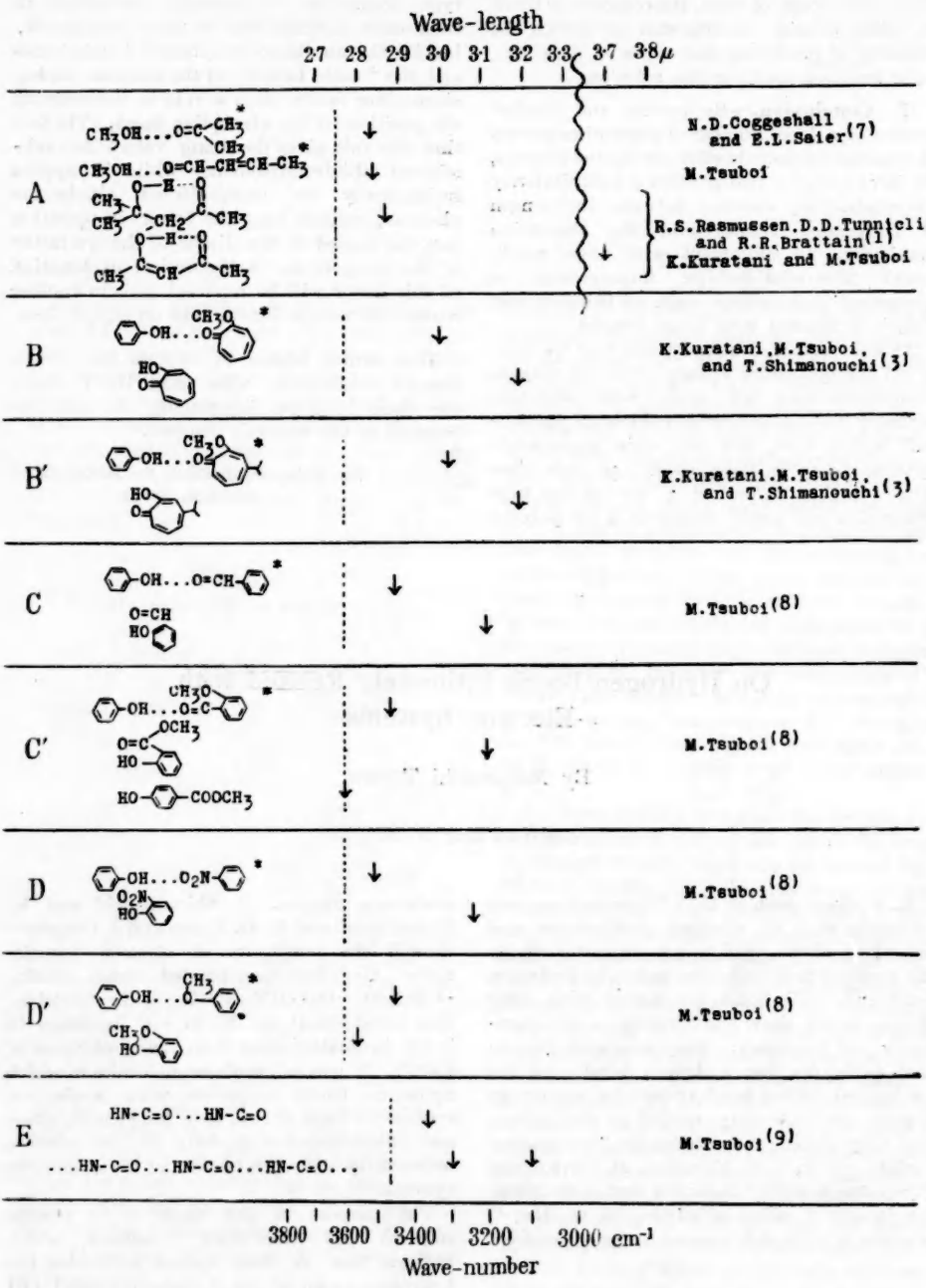


Fig. 1.

(7) N. D. Coggeshall and E. L. Saier. *J. Am. Chem. Soc*, **73**. 5414 (1951).
(8) M. Tsuboi, This Bulletin, **25**, 60 (1952).
(9) M. Tsuboi, This Bulletin, **22**, 215, 255 (1949).

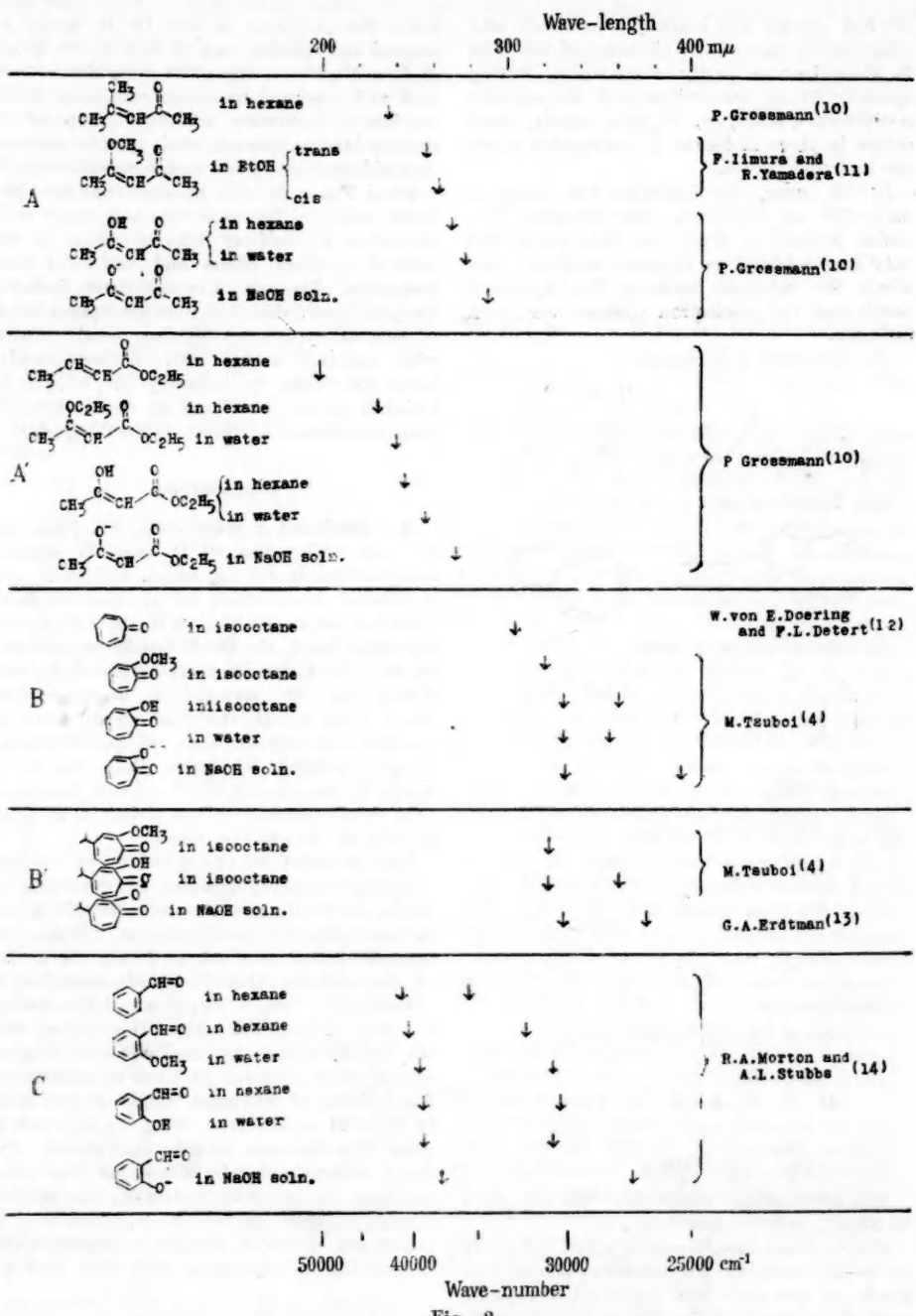


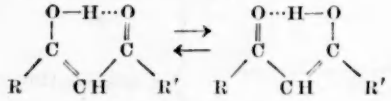
Fig. 2.

(10) P. Grossmann, *Z. Physik. Chem.*, **109**. 305 (1924).
(11) F. Iimura and R. Yamadera. Private communications.
(12) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**. 876 (1951).
(13) G. A. Erdtman, *Acta Chemica Scandinavica*, **4**, 1081 (1950).
(14) R. A. Mortman and A. L. Stubbs. *J. Chem. Soc.*, **1940**, 1347.

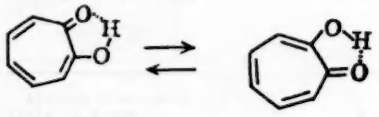
or NH groups are halfway dissociated and consequently two of the electrons of the O or N atom become partly π-electronic, having specially strong interactions with the adjacent π-electron systems, or, in other words, there occurs in these molecules a conjugation across the hydrogen bonds.

In this paper, the following five kinds of molecules are discussed. The resonance formulas tentatively given for these molecules may be considered to represent extreme cases where the relations between the hydrogen bonds and the π-electron systems are most intimate.

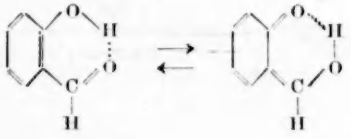
(A) Enolized β-diketones



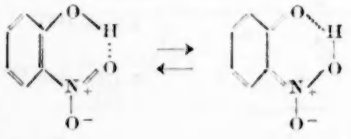
(B) Tropolone, etc.



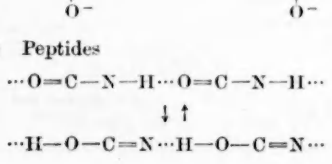
(C) Salicyl aldehyde, etc.



(D) *o*-Nitrophenol



(E) Peptides



Data

The infrared and ultraviolet data are given in Figs. 1 and 2 respectively.

Fig. 1 shows the degrees in which the O—H or N—H bonds in the above-mentioned five kinds of molecules are weakened compared with the normally hydrogen-bonded O—H or N—H bonds. The arrows in the figure indicate the positions of the infrared absorption bands due to the vibrations of O—H's and N—H's in various hydrogen-bonded states, and the dotted lines, the positions of free O—H bands of alcohol and phenol and of free N—H bands of N-methylacetamide. The formulas with * in Fig. 1 represent molecular complexes which are formed in ternary solutions composed of proton-donator (phenol, etc.), proton-acceptor (benzaldehyde, etc.), and carbon tetrachloride.[8]

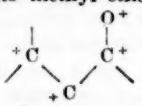
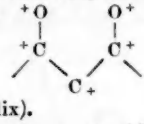
From Fig. 2, it may be seen that the electronic bands of the molecules now under consideration lie halfway between those of the methyl (or ethyl) ethers and anions of these molecules. The arrows in the figure indicate the positions of the ultraviolet absorption bands of several conjugated double bond systems with carbonyl groups. All of these bands, being too strong in intensity ($\varepsilon \doteqdot 10^4$) to be assigned to the transitions of $N \rightarrow E_n$ type,[15] may be assigned to those of $N \rightarrow V_n$ type.[15]

Discussions

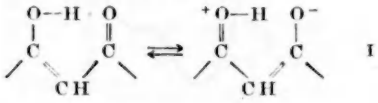
A. Enolized β-diketones. (Cf. Figs. 1A, 2A and 2A') — The O—H band of enolized acetylacetone is diffuse, broad, and weak, and is situated at a position (3.7 μ), much displaced from the proper position of O—H (2.75 μ). On the other hand, the O—H bands in ordinary O—H···O=C bondings are rather sharp and strong, and are situated at about 2.85 μ. These facts reveal that the O—H bond in enolized acetylacetone (one of the conjugated chelate systems) is weaker than the O—H bonds in the normal O—H···O=C bondings. (The force constant of the former is as small as 60% of that of the latter).

The so-called $N \rightarrow V_1$ band[15] of enolized acetylacetone methyl ether, a compound in which the OCH_3 group replaces the CH_3 group in mesityloxyde, is situated at 260 mμ the position shifted as much as 25 mμ from that of the corresponding band of mesityloxyde (235 mμ)[16]. The $N \rightarrow V_1$ band shifts further to about 270 mμ when the OH group replaces the OCH_3 group in enolized acetylacetone methyl ether to form enolized acetylacetone. The shifting of electronic bands due to mere $OCH_3 \rightarrow OH$ replacement being usually not so great (for instance anisole and phenol give their electronic bands almost at the same positions in nonpolar solvents), the above-mentioned shift of the $N \rightarrow V_1$ band may be something special in electronic structure. It is noteworthy in connection with this that the

(15) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).
(16) This shift may be due to the electron migration from the OCH_3 toward the π-electron system of the enolized acetylacetone methyl ether. See K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947); H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, **72**, 72, 74 (1951).

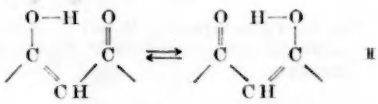
N→V$_1$ band of enolized acetylacetone is situated at an intermediate position between the bands of its methyl ether and its anion. This fact shows that the enolized acetylacetone is intermediate in the electronic state between its methyl ether and its anion; its methyl ether being composed of the field  and four π-electrons, and its anion composed of the field  and six π-electrons (see Appendix).

R. S. Rasmussen et al[1] assumed a resonance:



I

to occur in enolized acetylacetone. No evidence is contradictory to this theory, but the present writer is inclined to attach importance to the resonance:



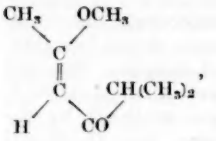
II

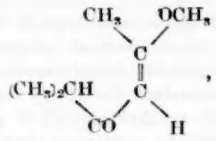
Thus, in the writer's view, the hydrogen atom is situated on the perpendicular bisector of the line connecting the two oxygen atoms, and the molecule has a symmetry plane which involves the bisector and is perpendicular to the molecular plane. Facts which favour the preference of resonance II rather than resonance I are:

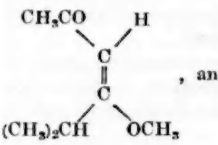
(i) The observed dipole moment of enolized acetylacetone (about 3 D. U.) is much smaller than it should be if resonance I were predominant.[17]

(ii) Infrared absorption band due to the O—H stretching vibration of this molecule is abnormally weak in intensity.

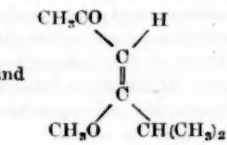
(iii) $CH_3C(OCH_3)=CH-CO-CH(CH_3)_2$ has four isomers,







and



while $CH_3C(OH)=CH-CO-CH(CH_3)_2$ has only one[11].

B. Tropolone, etc. (Cf. Fig. 1B, 1B′, 2B and 2B′) — Phenol-tropolone methyl ether, a complex with *inter*-molecular O—H···O=C bonding, gives its O—H band at 3.00 μ. Here, the carbonyl O of O—H···O=C bonding is considered to be situated on the prolongation of the line representing the O—H bond vector. On the other hand in tropolone, with *intra*-molecular O—H···O=C bonding, the position of the carbonyl oxygen atom deviates greatly from the prolongation of the O—H bond vector line. Merely from molecular geometrical considerations, the above facts might appear to show that the intramolecular O—H···O=C bonding of tropolone must be much weaker than the intermolecular O—H···O=C bonding between phenol and tropolone methyl ether, and accordingly that the O—H band must be situated at much shorter wave-length than 3.00 μ. However, the actually observed O—H band of tropolone in carbon tetrachloride is situated at 3.19 μ, much longer wavelength than 3.00 μ, and is weaker and broader than the above 3.00 μ band[3]. This is an indication that the O—H bond in tropolone is weakened under a special circumstance due to the intimate relation between the O—H···O bonding and the conjugated double bonds in the seven-membered ring.

The ultraviolet absorption spectrum of tropolone exhibits features intermediate between those of tropolone methyl ether and tropolone anion. This may be taken as indicating that the intramolecular hydrogen bonding in tropolone gives an effect upon tropone ring to transform its electronic structure halfway toward that of tropolone anion.

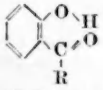
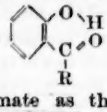
As may be seen from Fig. 1B′ and 2B′ the O—H···O bonding in hinokitiol is the same in nature as that of tropolone.

C. Salicyl aldehyde, etc. (Cf. Fig. 1C, 1C′, and 2C)—The O—H bands of salicyl aldehyde and methyl salicylate are situated

(17) According to J. B. Conant and A. F. Thompson (*J. Am. Chem. Soc.*, **54**, 4039 (1932)), keto-enol equilibrium in β-diketones shifts toward keto-form in polar solvents, and toward enol-form in nonpolar solvents, indicating that the enol-form of β-diketones is in general less polar than the keto-form. According to C. T. Zahn (*Physik. Z.*, **34**, 870 (1933)) the mean dipole moment of acetylacetone molecule is 3 D. U. in gas phase, where more than 90% of molecules take the enol-form.

at longer wave-lengths respectively than those of intermolecular complexes: phenol-benzaldehyde and phenol—methyl benzoate. This fact shows that the O—H bond in salicyl aldehyde and methyl salicylate are weakened by the intimate relations between the O—H···O bondings and the conjugated double bond systems in these molecules.

Each of the ultraviolet absorption bands of salicyl aldehyde is intermediate in its position between the corresponding bands of its methyl ether and its anion.

A. E. Martin[18] found that in  type molecules a broad O—H band is associated with the structure where R is H or CH_3, but a sharp band is produced when R is OH or OCH_3. As is known, the OH and OCH_3 groups are lower in ionization potential than the alkyl groups[19]. Then, what Martin found may be expressed as follows: the relation between the hydrogen bond and the conjugated double bond system in  type molecules becomes less intimate as the ionization potential of R becomes lower.

D. *o*-Nitrophenol. (Cf. Fig. 1D and 1D′)—The shifting of the O—H band of phenol due to its forming an intermolecular hydrogen bond with nitrobenzene is only from 2.77 μ to 2.84 μ. From this it is seen that the oxygen atom of nitro group attached to the benzene ring is not a strong proton acceptor. Nevertheless, the O—H band of *o*-nitrophenol is situated at 3.08 μ, a much displaced position. Then, the intramolecular hydrogen bond in *o*-nitrophenol must also be related intimately with the π-electron system*.

E. Peptides. (Cf. Fig. 1E)—The dimer of N-methylacetamide with a single N—H···O=C bonding gives one N—H association bands at 2.97 μ, while its *long* chain polymer gives two N—H association bands at 3.03 μ and 3.22 μ[9]. This fact is considered to have some connections with the view advanced by T. Shimanouchi and S. Mizushima[5] as well as by M. G. Evans and J. Gergely[6], that a "conjugation"[20] is possible along the hydrogen-bonded long chain, ···HN—C=O··· HN—C=O···, in protein.

The appearance of the second N—H band at 3.22 μ is characteristic of this system. Recently, I. Oshida and Y. Oshika,[21] showed theoretically that, if in a hydrogen bond, X—H···Y, there are two almost equally stable positions of the proton between the two atoms X and Y, and if the potential barriers between these two stable positions are of certain appropriate height (Fig. 3, A), there must occur two bands in the 3 μ region from this system.

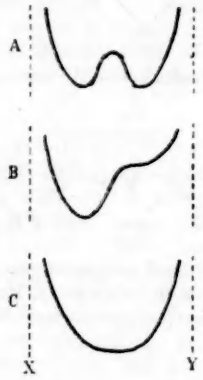
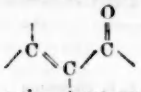
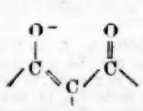


Fig. 3.—Three types (A, B and C) of the potential curve of proton in X—H···Y bonding.

It is possible that the two N—H bands of the N—H···O bondings in the long chain, ···HN —C=O···HN—C=O···, and in the ring dimers of δ-valerolactam[9],[22], ε-caprolactam[9] and diketopiperazine[9] correspond to the theoretically expected bands. Further, it is possible that in ordinary hydrogen bonds one of the potential valley is much deeper than the other (Fig. 3, B) and in the conjugated chelate system there is only one wide potential valley near the centre of the line connecting X and Y atoms (Fig. 3, C).

Appendix

Electronic states of acrolein type molecule  and enolized acetylacetone anion type molecule  will be

(18) A. E. Martin, *Nature*, **166**, 474 (1950).
(19) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).
(20) H. C. Longuet-Higgins and G. W. Wheland, *Annual Rev. Phys. Chem.*, **1**, 133 (1949).
* The O-H band due to the intramolecular hydrogen bond not related with the π-electron system is situated at a position not much displaced from 2.77μ, as is exemplified by guaiacol which gives an O-H band at 2.80μ. (Cf. Fig. 1 D,).

(21) I. Oshida and Y. Oshika, *Bussei-ron Kenkyu*, **46**, 95 (1952).
(22) M. Tsuboi, This Bulletin, **24**, 75 (1951).

treated here according to the simple molecular orbital methods.

(I) Treatment by the LCAO Method.—Neglecting the overlap integrals, we can write the secular equation for the approximate molecular orbitals, which may be expressed as linear combinations of $2p\pi$ atomic orbitals of the C and O atoms composing these molecules, in the form:

$$\begin{vmatrix} \alpha_O-E & \gamma_{CO} & 0 & 0 \\ \gamma_{CO} & \alpha_C-E & \gamma_{CC} & 0 \\ 0 & \gamma_{CC} & \alpha_C-E & \gamma_{CC} \\ 0 & 0 & \gamma_{CC} & \alpha_C-E \end{vmatrix} = 0 \text{(acrolein)},$$

$$\begin{vmatrix} \alpha_O-E' & \gamma_{CO} & 0 & 0 & 0 \\ \gamma_{CO} & \alpha_C-E' & \gamma_{CC} & 0 & 0 \\ 0 & \gamma_{CC} & \alpha_C-E' & \gamma_{CC} & 0 \\ 0 & 0 & \gamma_{CC} & \alpha_C-E' & \gamma_{CO} \\ 0 & 0 & 0 & \gamma_{CO} & \alpha_O-E' \end{vmatrix} = 0$$

(enolized acetylacetone anion)

where α_C and α_O are the Coulomb terms for the C and O atoms, and γ_{CC} and γ_{CO} are the resonance integrals of the adjacent C—C and C—O respectively. If we assume, according to M. J. S. Dewar,[23] that

$$\alpha_C-\alpha_O=\beta$$
$$\gamma_{CO}=\sqrt{2}\beta$$
$$\gamma_{CC}=\beta \qquad \beta=-73.2 \text{ kcal./mol.} \quad (25600 \text{ cm.}^{-1}),$$

we obtain the following values for energy levels of the π-electrons:

$$E=\alpha_C-2.22\beta,\ \alpha_C-\beta,\ \alpha_C+0.45\beta,\ \alpha_C+1.67\beta \text{ (acrolein)}$$
$$E'=\alpha_C-2.34\beta,\ \alpha_C-2\beta,\ \alpha_C-0.47\beta,\ \alpha_C+\beta,\ \alpha_C+1.81\beta$$
(enolized acetylacetone anion).

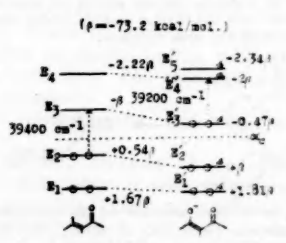
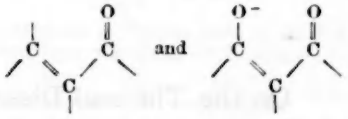


Fig. 4.

These energy levels are shown graphically in Fig. 4, in which s or a designates whether the wave function belonging to the level is symmetrical or antisymmetrical with respect to the symmetry plane of enolized acetylacetone anion molecule, which is perpendicular to the molecular plane. The observed 235 mμ (42600 cm.$^{-1}$) band of mesityloxyde may correspond to the $E_2 \rightarrow E_3$ transition (See Fig. 4, calculated 39400 cm.$^{-1}$), and the observed 290 mμ (34500 cm.$^{-1}$) band of enolized acetylacetone anion to the $E_3' \rightarrow E_4'$ transition (See Fig. 4, calculated 39200 cm.$^{-1}$).

(II) Treatment by the Free Electron Model Method.—The method assumes a model where the π-electrons in the systems



are one-dimensional electron-gases in the fields, A and B, of uniform potential, whose lengths are x and y respectively. | A | ←x→ | B | ←y→ The solution[24] of the Schrödinger equation for this model gives the energy levels shown in Fig. 5, and based on this, the wave-numbers

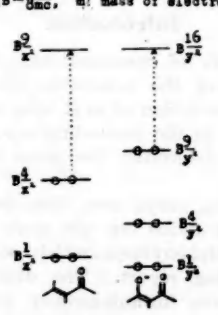


Fig. 5.

of the $N \rightarrow V_1$ bands of acrolein and enolized acetylacetone anion should be

$$\nu_1 = B\frac{5}{x^2} \quad \text{and} \quad \nu'_1 = B\frac{7}{y^2}$$

respectively. If we put here

$$\frac{x}{y} = \frac{3}{4}$$

(23) M. J. S. Dewar, *J. Chem. Soc.*, **1950**, 2329.

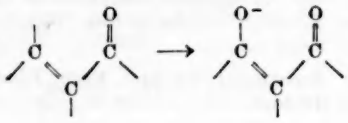
(24) N. S. Baylis, *J. Chem. Phys.*, **16**, 287 (1948).

then $$\frac{\nu_1}{\nu_1'} \fallingdotseq \frac{5}{4}$$

This is in agreement with the observed ratio,

$$\frac{\nu_{obs.}}{\nu'_{obs.}} = \frac{42600\ \text{cm.}^{-1}}{34500\ \text{cm.}^{-1}} \fallingdotseq \frac{5}{4}.$$

This agreement shows that the magnitude of red-shift of the $N \rightarrow V_1$ band due to the change:



may be well explained on the basis of the free electron model.

The writer wishes to express his sincere thanks to Professors Sanichiro Mizushima, Takehiko Shimanouchi, and Saburo Nagakura, and to Mr. Hiroaki Baba, for their kind guidance and valuable suggestions. The expense of this research has been partly defrayed from Grant in Aid for Scientific Research from Ministry of Education.

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On the Thermal Dissociation of Organic Compounds. II. The Dissociation of the Urea Linkage in Sym-dimethylurea, Asym-dimethylurea and Asym-phenylethylurea in Butyric Acid

By Toshio Hoshino, Teruaki Mukaiyama and Hiroko Hoshino

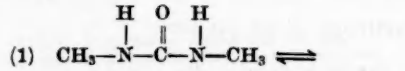
(Received April 28, 1952)

Introduction

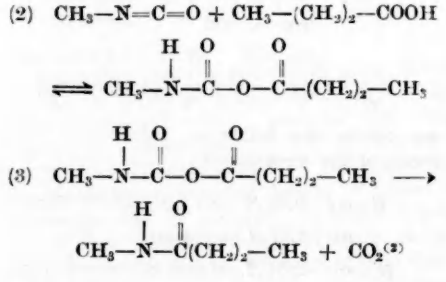
The results of measurements of the rate constants and the activation energy of the thermal dissociation of aryl urea have already been shown in the preceeding report.[1] Then we tried to determine the same constants in alkyl urea.

On heating, alkyl urea dissociates to isocyanate and amine by the same mechanism as in sym-diphenylurea which was shown in the preceeding report. The dissociated isocyanate reacts instantaneously with butyric acid which was used as solvent and forms carbaminic acid-butyric acid-anhydride and then easily decomposes to butyrated amine and carbon dioxide.

The thermal dissociation of sym-dimethylurea in butyric acid involves the following reactions:



(1) $CH_3-N(H)-C(=O)-N(H)-CH_3 \rightleftharpoons CH_3-N=C=O + CH_3-NH_2$

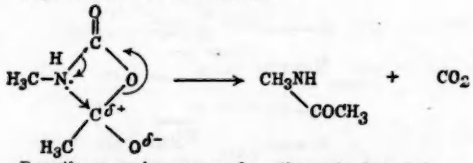


(2) $CH_3-N=C=O + CH_3-(CH_2)_2-COOH \rightleftharpoons CH_3-N(H)-C(=O)-O-C(=O)-(CH_2)_2-CH_3$

(3) $CH_3-N(H)-C(=O)-O-C(=O)-(CH_2)_2-CH_3 \longrightarrow CH_3-N(H)-C(=O)(CH_2)_2-CH_3 + CO_2$[2]

(1) T. Hoshino, T. Mukaiyama and H. Hoshino, *J. Am. Chem. Soc.*, **74**, 3097 (1952).

(2) The mechanism of process (3) can be considered as follows;. Conceivably it will proceed by way of an intramolecular nucleophilic displacement as sketched below. The use of isotropic carbon should be serviceable to demonstrate that the carbon dioxide which was evolved originated from the urea molecule.



Recently, as we have assumed on the mechanism of the decarboxylation of anhydride of carbamic and fatty acids, it was proved[2]' by using C^{13} atom that carbon dioxide which was evolved originated from the urea molecule.

(2)' H. R. V. Arnstein and Ronald Bentley, *J. Chem. Soc.*, **1951**, 3509.

(4) $CH_3-NH_2 + CH_3-(CH_2)_2-COOH \rightleftharpoons CH_3-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-(CH_2)_2-CH_3 + H_2O.$

If reaction (1) is rate-determining, the rate of dissociation becomes measurable if one determines the amount of carbon dioxide evolved according to (3).

Unlike the case of sym-diphenylurea described in the previous report, sym-dimethylurea could not be dissociated in acetic acid even at the boiling point (118°C), so butyric acid was adopted as the solvent and the reaction was carried above 130°C.

Asym-dimethylurea and asym-phenylethylurea dissociate, respectively, to dimethylamine and isocyanic acid, phenylethylamin and isocyanic acid in acetic acid. It was found that the reactions are similar to the case of sym-diphenylurea in acetic acid as shown in the first report. The dissociation reaction and the reaction of isocyanic acid with acetic acid proceed at comparable rate.

The rate constants and the activation energy of thermal dissociation in butyric acid were derermined.

Experimental Part

A 35 ml. long-necked, round-bottomed flask was connected to a gas buret by means of a capillary tube. Halfway along the capillary tube, a 10 ml. bulb was inserted which was maintained at 0°C. to condense reaction products less volatile than carbon dioxide. The reaction vessel was maintained at a desired, constant temperature by immersion into the vapors above a suitable boiling liquid contained in a three-necked flask equipped with condenser and thermometer; the reaction vessel was inserted in the centre neck of the flask. Vapors of the following liquid were used as heating agents: water, isoamylalcohol, xylene and anisole. The liquid was distilled prior to each run; during the course of an experiment (one to two hours) the temperature remained satisfactorily constant as long as the atmospheric pressure did not fluctuate.

Sym-dimethylurea (m. p. 108.5°C.), asym-dimethylurea (m. p. 181.0°C.) and asym-phenylethylurea (m. p. 60~61°C.) were used. Acetic acid was distilled after prolonged boiling with acetic anhydride. Butyric acid was carefully purified by vacuum distillation.

The ratio of urea to fatty acid was 1 mole: 100 moles.

To compute the rate constant of the reaction of the thermal dissociation of urea, we have used the following treatment. The first order rate law can be expressed as

$$Y = A(1-e^{-kt}), \qquad (1)$$

in which A is initial concentration of urea and Y is the amount of dissociated urea at any time. Therefore

$$\ln \Delta Y = [\ln A + \ln(1-e^{-k\Delta t})] - kt. \qquad (2)$$

As $[\ln A + \ln(1-e^{-k\Delta t})]$ is considered as independent term with respect to t, equation (2) can be expressed as follows;

$$\ln \Delta Y = \text{Constant} - kt$$

For the reaction of the first order, it requires the plot of $\ln \Delta Y$ against t to be a straight line. The rate constant is given by the gradient of the $t-\ln \Delta Y$ diagram shown in the Fig. 1, 3, and 5. For example, the experiment gave the following results. (Table 1, 2 and 3) Thermal dissociation of sym-dimethylurea in butyric acid.

Table 1

Sym-dimethylurea in Butyric Acid at 409.0°K.
Calculated with the Value of $\Delta t = 60$ min.

time (min.)	CO_2 evolved(cc.)	time (min.)	CO_2 evolved(cc.)	ΔY
10	4.2	70	24.0	19.8
15	6.1	75	25.3	19.2
20	8.1	80	26.7	18.6
25	9.9	85	27.9	18.0
30	11.6	90	29.3	17.7
35	13.3	95	30.5	17.2
40	15.0	100	31.7	16.7
45	16.6	105	32.9	16.3
50	18.2	110	34.0	15.8
55	19.7	115	35.0	15.3
60	21.2	120	36.1	14.9
65	22.6	125	37.2	14.6

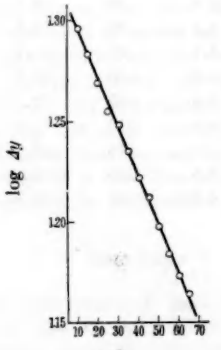


Fig. 1.—The plot of t against $\log \Delta Y$. Sym-dimethylurea in butyric acid at 409.0°K.

First order kinetics with respect to sym-dimethylurea was observed.

The rate constant (min.$^{-1}$)

$T = 409.0$°K. $k = 5.64 \times 10^{-3}$
$T = 413.2$°K. $k = 8.42 \times 10^{-3}$
$T = 421.5$°K. $k = 1.62 \times 10^{-2}$

The activation energy

$E = 34.3$ kcal.

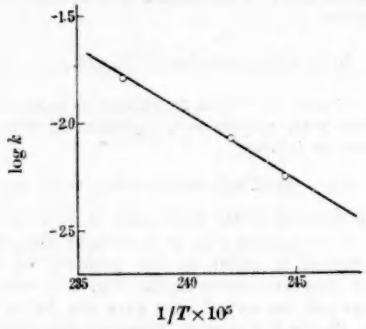


Fig. 2.—Thermal dissociation of sym-dimethylurea in butyric acid: the plot of $1/T$ against $\log k$.

It may be noted again that the thermal dissociation of sym-dimethylurea does not occur in acetic acid.

Thermal dissociation of asym-dimethylurea in butyric acid.

Table 2

Asym-dimethylurea in Butyric Acid at 402.8°K. Calculated with Value of $\Delta t = 60$ min.

time (min.)	CO_2 evolved (c.c.)	time (min.)	CO_2 evolved (c.c.)	ΔY
10	1.4	70	8.7	7.3
15	2.0	75	9.2	7.2
20	2.8	80	9.8	7.0
25	3.4	85	10.3	6.9
30	4.1	90	10.8	6.7
35	4.7	95	11.2	6.5
40	5.2	100	11.7	6.5
45	5.8	105	12.2	6.4
50	6.4	110	12.6	6.2
55	7.0	115	13.1	6.1
60	7.5	120	13.5	6.0
65	8.2	125	13.9	5.7

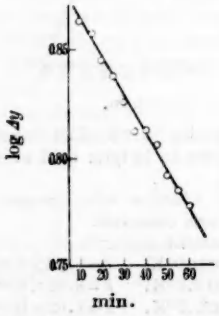


Fig. 3.—The plot of t against $\log \Delta Y$. Asym-dimetylurea in butyric acid. at 402.8°K.

First order kinetics with respect to asym-dimethylurea was observed.

The rate constant (min.$^{-1}$)

$T = 402.8$°K. $\quad k = 3.98 \times 10^{-3}$

$T = 409.0$°K. $\quad k = 5.94 \times 10^{-3}$

$T = 422.0$°K. $\quad k = 1.70 \times 10^{-2}$

The activation energy

$E = 26.7$ kcal.

When asym-dimethylurea is heated in acetic acid, the result does not satisfy the requirement for first order kinetics. As shown in Fig. 4, the reaction belongs to the successive one.

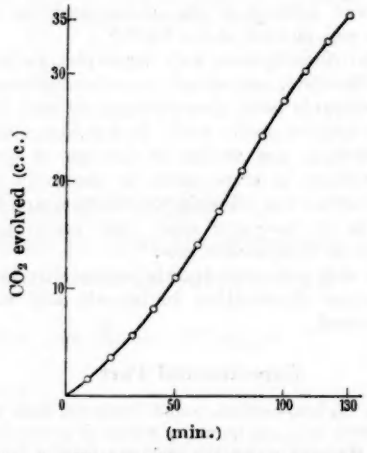


Fig. 4.—Thermal dissociation of asym-dimethylurea in acetic acid at 372.1°K.

The thermal dissociation of asym-phenylethylurea in butyric acid.

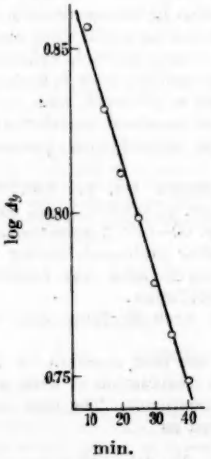


Fig. 5.—The plot of t against $\log \Delta Y$. Asym-phenylethylurea in butyric acid at 409.8°K.

Table 3

Asym-phenylethylurea in Butyric Acid at 409.8°K., Calculated with the Value of $\Delta t = 35$ min.

time (min.)	CO_2 evolved(c.c.)	time (min.)	CO_2 evolved(c.c.)	ΔY
10	1.4	45	8.6	7.2
15	2.7	50	9.5	6.8
20	3.9	55	10.4	6.5
25	4.9	60	11.2	6.3
30	5.9	65	11.9	6.0
35	6.9	70	12.7	5.8
40	7.8	75	13.4	5.6

First order kinetics with respect to asym-phenylethylurea were observed.

The rate constant ($min.^{-1}$)

$T = 400.5°K.$ $k = 1.47 \times 10^{-3}$

$T = 409.8°K.$ $k = 4.07 \times 10^{-3}$

$T = 411.8°K.$ $k = 4.93 \times 10^{-2}$

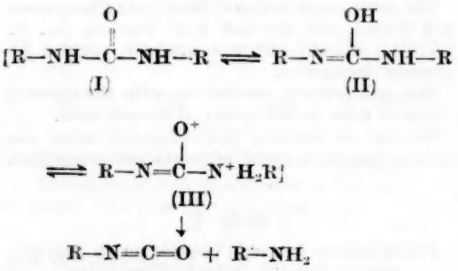
The activation energy

$E = 30.2$ kcal.

When asym-phenylethylurea is heated in acetic acid, the result was similar to that described in the case of asym-dimethylurea in acetic acid.

Discussion

The dissociation of urea may be considered to proceed over tautomerizations:



As the tautomerization occurs by an intramolecular proton transfer, the ability of proton-donors or proton-acceptors of nitrogen of urea is considered as one of the important factors for the reaction to proceed. In the tautomerization above mentioned, the tautomer (III) may be considered as activated state, which ready to dissociate into isocyanate and amine.

Experiment shows that the activation energy of sym-dimethylurea (34.3 kcal.) is larger than that of sym-diphenylurea (28.0 kcal.). By resonance effect of phenyl group, the basic strength of aromatic amine is less than that of alkyl amine as shown in Table 4 by pKh values. The tautomer (II) formed in sym-diphenylurea has more tendency to dissociate proton than in sym-dimethylurea which will be proportional to the basic charactor of corresponding amines. Also, when the tautomer (III) is formed the stability of dissociated products in arylurea introduced by resonance energy will promote the reaction more than in alkylurea. Consequently, the dissociation reaction of alkylurea needs more energy than that of arylurea.

Table 4

The pKh value for amines reported by Hall and Sprinkle[3]

ammonia	9.27	dimethylamine	10.71
methylamine	10.64	phenylethylamine	5.11
aniline	4.62		

The activation energy of asym-dimethylurea (26.7 kcal.) is smaller than that of sym-dimethylurea. In case of asym-dimethylureas, one nitrogen of urea is the primary and the other is the tertiary. In asym-dimethylureas, the tautomer (II) has more tendency to dissociate proton and to accept proton in the tautomer (III). These considerations are deduced from the basic strength of the corresponding amines. By these two effects, the reason for the lower activation energy of dissociation can be explained.

The activation energy of asym-phenylethylurea (30.2 kcal.) is larger than that of asym-dimethylurea. In these ureas, the ability of dissociating proton from the tautomer (II) is the same and that of accepting proton in the tautomer (III) is different. The tertiary nitrogen of asym-phenylethylurea has aliphatic- and phenyl-groups. By the resonance effect of the phenyl-group, the basic strength decreased as compared with that in asym-dimethylurea. Consequently, it is clear that the larger activation energy will be required.

Summary

(1) The rate constants and the activation energies of the thermal dissociation of sym-dimethylurea, asym-dimethylurea and asym-phenylethylurea were determined.

(2) It was demonstrated that the substituents have great influence on the dissociation reaction.

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(3) Norris F. Hall and Marshall R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

On the Thermal Dissociation of Organic Compounds. III. The Dissociation of Ester Linkage in Phenylcarbaminic acid phenylester in Butyric acid.

By Toshio Hoshino, Teruaki Mukaiyama and Hiroko Hoshino

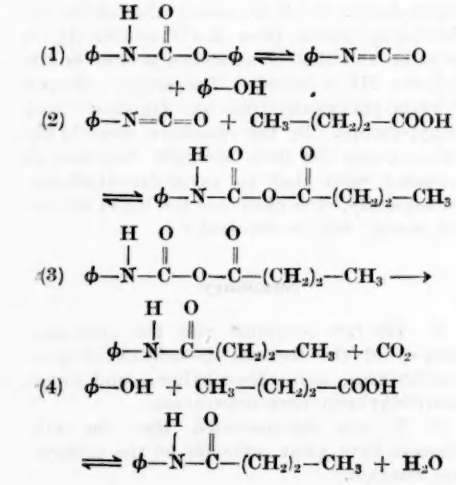
(Received April 28, 1952)

Introduction

That phenylcarbaminic acid phenylester decomposes to phenyisocyanate and phenol on heating has already been reported.[1] It can be considered, that the carbaminic acid ester linkage of phenylcarbaminic acid phenylester dissociates to phenylisocyanate and phenol by the same mechanism as described in the preceding report[2][3] in the urea linkage which showed that it dissociates to isocyanate and amine.

In the present work, we tried to determine the rate constant and the activation energy of dissociation by the same method used in the thermal dissociation of urea linkage.

The thermal dissociation of phenylcarbaminic acid phenylester in butyric acid involves the following reactions:



Even at the boiling point of acetic acid, the thermal dissociation of ester linkage of phenylester could not be observed. Then ester was heated in butyric acid and the dissociation reaction was observed above 130°.

As the rate of reaction of the isocyanate dissociated with butyric acid is thirty times faster than that of dissociation as it was observed by our previous experiment, we were able to determine the rate constant and the activation energy of dissociation of ester by measuring the volume of carbon dioxide evolved throughout the reaction.

Experiment Part

The apparatus was the same as that described in the first report and the volume of carbon dioxide evolved during the reaction was measured.

The sample was prepared from phenylisocyanate and phenol, recrystallized from alcohol. (m. p. 127.0°C.) Butyric acid was carefully purified by vacuum distillation.

The reaction was carried out with the ratios of 1mole of ester to 100 moles of butyric acid.

The rate of reaction was computed using the same procedure as described in the previous report.

Table 1

Phenylcarbaminic acid phenylester in butyric acid at 409.1°K, calculated with the value of $\Delta t = 50$ min.

time (min.)	CO_2 evolved(cc.)	time (min.)	CO_2 evolved(cc.)	ΔY
10	6.2	60	28.7	22.5
15	9.3	65	30.5	21.2
20	12.0	70	32.0	20.0
25	14.2	75	33.7	19.5
30	16.5	80	35.2	18.7
35	18.7	85	36.4	17.7
40	20.7	90	37.6	16.9
45	22.9	95	38.8	15.9
50	24.9	100	39.7	14.8
55	26.7	105	40.6	13.9

The rate satisfied the requirement for first order kinetics with respect to the ester.

(1) E. Lenckart, *J. prakt. Chem.*, **41**, 318 (1890).
(2) T. Hoshino, T. Mukaiyama and H. Hoshino, *J. Am Chem. Soc.*, **74**, 3097 (1952).
(3) T. Hoshino, T. Mukaiyama and H. Hoshino, This Bulletin, **25**, 392 (1952).

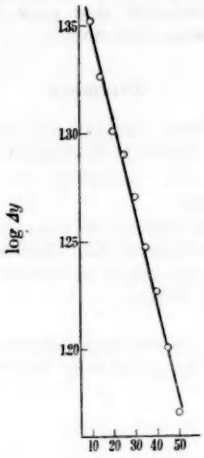


Fig. 1.—The plot of t against $\log \Delta Y$. Phenylcarbaminic acid phenylester in butyric acid at 409.1°K.

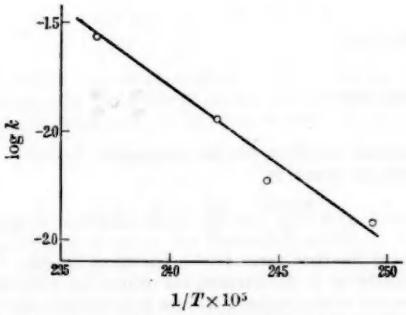


Fig. 2.—Thermal dissociation of phenylcarbaminic acid phenylester in butyric acid: the plot of $1/T$ against $\log k$.

The rate constant (min.$^{-1}$)

$T=401.1$°K. $k=3.98\times10^{-3}$
$T=409.1$°K. $k=5.94\times10^{-3}$
$T=413.0$°K. $k=1.23\times10^{-2}$
$T=422.6$°K. $k=2.71\times10^{-2}$

The activation energy

$E=33.3$ kcal.

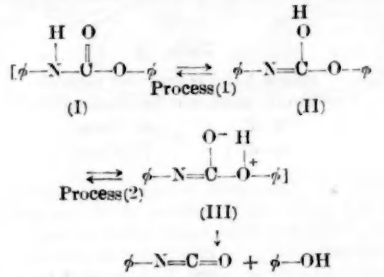
It may be noted again that the thermal dissociation of ester does not occur in acetic acid even at the boiling point.

Discussion

As the result of the experiment, the activation energy of thermal dissociation of ester is shown to be larger than that of urea. This explains the fact that the dissociation of ester does not occur even at the boiling point of acetic acid.

The activation energy of dissociation of diphenylurea in butyric acid is 28.0 kcal. and that of phenylcarbaminic acid phenylester is 33.3 kcal.. This difference between the two substances can be explained by the following considerations.

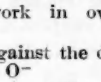
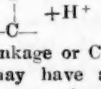
In phenylcarbaminic acid phenylester, it may be shown that the equilibrium will take place between (II) and (III) by a intramolecular proton transfer. The equilibrium shifts in the direction of (II) and (III) on heating. The (III) dissociates to phenol and phenylisocyanate.



The urea, as shown in the first report, dissociates by the same mechanism.

The difference of the activation energies required for dissociation between urea and ester will be explained by using the terms, "chemical driving force" and "chemical inertia," introduced by Evans and Polanyi[4]. In the tautomerization above mentioned, (III) may be considered as activated state, which is ready to dissociate into isocyanate and alcohol. The difference between urea and ester may depend on process (2), because no appreciable difference can be found in process (1).

With the aid of this consideration, the energy required for dissociation depends on the following factors.

The chemical inertia may be attributed to the work in overcoming the interference action against the dissociating proton from  to  and to that breaking the C—O linkage or C—N linkage. These two compounds may have a similar tendency for the former factor. According to Pauling[5] the bond energy of C—N linkage is smaller than that of C—O linkage as shown in Table 2. In this case, however, instead of neutral atoms, they should be considered as C—N$^+\rightarrow$C$^+$:N or C—O$^+\rightarrow$C$^+$:O, and the numerical values can not be designated exactly. These considerations suggest that the chemical inertia of ester is larger than that of urea.

The chemical driving force necessary for the rupture of the ester or urea linkages may be

(4) Reviewed by Evans and Polanyi, *Trans. Fard. Soc.*, **34**, 11. (1938).

(5) L. Pauling, "The nature of the Chemical Bond", Cornell University Press, 1939, p. 57.

attributed to the formation of alcohol or amine. The heat of formation of aniline from $H^+ + -\overset{H}{\underset{..}{N}}-\phi$ or phenol from $H^+ + -\ddot{O}\phi$ and the proton acceptability of nitrogen of urea or oxygen of ester are considered as the chemical driving force in these reactions. The basity of aniline is much larger than that of phenol and this suggests that the chemical driving force is larger in urea than in ester.

The difference of the chemical inertia and the chemical driving force is the necessary potential energy of activation. On these considerations, it can be concluded that ester requires more activation energy than urea.

Table 2

Single bond energy for neutral atoms as shown by Pauling[5]	
N—C	48.6 kcal.
O—C	70.0 kcal.

Summary

(1) The rate constant and the activation energy of thermal dissociation of phenylcarbaminic acid phenylester in butyric acid are determined.

(2) It has been made clear on the basis of reaction mechanism that dissociation of ester linkage requires larger activation energy than that of urea linkage.

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Theory of Monolayer. I. Heat of Surface Vaporization in the Monolayer

By Hiroshi HOTTA

(Received April 28, 1952)

The estimation of the heat of surface vaporization in the monolayer has been tried by several investigators by applying the two-dimensional Clapeyron-Clausius' equation.[1],[2] For the estimation by this method, however, we must have both the knowledge of the area occupied by a molecule in the gaseous film as well as in the liquid film at the transition pressure, and the knowledge of the temperature depend ence of the transition pressure. These measurements are experimentally not very simple. However, the new method presented here provides the information on the heat of surface vaporization in the monolayer without any experimental difficulty.

In general the free volume in a liquid can be estimated from the vapour pressure.[3] Conversely the heat of surface vaporization must be obtained by the definition of the free surface area from a surface pressure-area curve as follows. For this purpose we shall begin with the construction of the partition function. The molecular[4] complete partition function for the monolayer, f, would be given as usual by

$$f = \frac{2\pi mkT}{h^2} \times \frac{kT}{h\nu} \times j(T) \times \Omega(T), \qquad (1)$$

where the first term is the partition function for translation in the surface, the second for vibration normal to the surface, $j(T)$ for the internal degrees of freedom of the molecule in the surface, and $\Omega(T)$ for the configurational potential energy.

Since we can write $\Omega(T)$ for the perfect gaseous film in the form

$$\Omega(T) = A = \frac{kT}{F}, \qquad (2)$$

where A is the molecular surface area and F the surface pressure, the partition function (1) is rewritten as

$$f^G = \frac{2\pi m(kT)^2}{h^2 F^G} \cdot \frac{kT}{h\nu^G} \cdot j^G(T), \qquad (3)$$

where the superscript G refers to the gaseous film. On the other hand, $\Omega(T)$ for the liquid film can be expressed in the form

$$\Omega(T) = A_f e^{(U+kT)/kT}, \qquad (4)$$

according to the smoothed potential model[5], where U is the potential energy of the molecule when it is at the centre of its cell referred to an energy zero at infinite separation of the molecule,

(1) J. Sameshima, *Proc. Imp. Acad. Japan*, **10**, 153 (1934).
(2) N. K. Adam and G. Jessop, *Proc. Roy. Soc.*, **A 110**, 423 (1926).
(3) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," 1939, p. 332.
(4) Since only the molecular quantity is treated in this paper, the word "*molecular*" is omitted hereafter, as far as the omission does not cause confusion.
(5) Reference 3, p. 325.

A_f the free surface area, of which definition will be given in the later part of this paper. Then, the partition function (1) is rewritten as

$$f^L=\frac{2\pi mkTA_f}{h^2}\cdot\frac{kT}{h\nu^L}\cdot j^L(T)\cdot e^{(U+kT)/kT}, \quad (5)$$

where the superscript L refers to the liquid film.

Hence we have for the chemical potential, μ, as usual

$$\mu^G=-kT\log f^G$$
$$=kT\log F^G-kT\log\frac{2\pi m(kT)^2}{h^2}-kT\log\frac{kT}{h\nu^G}$$
$$-kT\log j^G(T), \quad (6)$$

and

$$\mu^L=-kT\log f^L+F^LA^L$$
$$=-U-kT-kT\log\frac{2\pi mkTA_f}{h^2}-kT\log\frac{kT}{h\nu^L}$$
$$-kT\log j^L(T)+F^LA^L. \quad (7)$$

The equilibrium condition between gaseous and liquid film is

$$\mu^G=\mu^L. \quad (8)$$

Hence, equating (6) and (7), and assuming $j(T)$ to be equal in both films we obtain

$$\frac{F^GA_f}{kT}\cdot\frac{\nu^L}{\nu^G}=e^{-\frac{U+kT-F^LA^L}{kT}}. \quad (9)$$

Furthermore, assuming ν to be equal in both films, the propriety of which will be criticised in the following paper, we can rewrite (9) as

$$\frac{F^GA_f}{kT}=e^{-\frac{U+kT-F^LA^L}{kT}}, \quad (10)$$

where all the quantities in (10) correspond of course to these at the transition point.

On the other hand, the heat content, H, is as usual

$$H^G=-T^2\left(\frac{\partial\mu^G/T}{\partial T}\right)_F$$
$$=2kT+E^G_{int}, \quad (11)$$
$$H^L=-T^2\left(\frac{\partial\mu^L/T}{\partial T}\right)_F$$
$$=-U+kT+E^L_{int}+F^LA^L. \quad (12)$$

If we assume the internal contribution, E_{int}, including the vibration normal to the surface, to be equal in both films, corresponding to the assumption for the equality of $j(T)$ and ν, the heat of surface vaporization L^v, is written as

$$L^v=H^G-H^L=U+kT-F^LA^L \quad (13)$$

Introducing this relation into (10), it becomes

$$\frac{F^GA_f}{kT}=e^{-\frac{L^v}{kT}}. \quad (14)$$

The larger the molecular area in the liquid film is, the more accurate this equation is, because the state is more ideal and it is assumed implicitly in the above derivation that the configuration of molecule in the surface is similar in both films. In this sense the following calculation listed in Table 1 is rational.

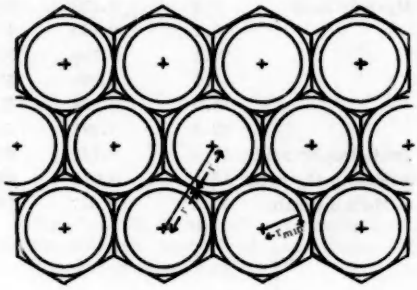

Fig. 1.

For the estimation of the heat of surface vaporization, it is necessary to define the free surface area with the measurable quantities. Since the molecules in the liquid film are supposed to be closely packed and each of them is free to move in each cell, the observed surface area may be the area of a hexagon as shown in Fig. 1. When the radius of an inscribed circle is r, the area must be

$$A=3.464\,r^2. \quad (15)$$

If it is supposed, that the minimum compressible surface area, A_{min}, *in this state* is equal to the area at the kink point for the next transition or at the collapse point, A_{min} is similarly expressed by

$$A_{min}=3.464\,r^2_{min}, \quad (16)$$

where r_{min} is the radius of an inscribed circle in this case. Therefore, the free surface area might be expressed by

$$A_f=3.464(2r-2r_{min})^2, \quad (17)$$

as the modification of a model used by Lennard-Jones and Devonshire.[6] Substituting from (15) and (16) into (17) we can obtain

$$A_f=4g(\sqrt{A}-\sqrt{A_{min}})^2, \quad (18)$$

where g is the form factor as the measure of the deviation of the chain molecule from the rigid disk model. Although there is no physical evidence that the hexagon model should be especially accepted to the free surface, this correction is also contained in this form factor. For simplicity, this factor is assumed hereafter to be unity even though it may be slightly more than unity.

We can now attain the first object by inserting (18) into (14), that is,

$$\frac{4F^G(\sqrt{A}-\sqrt{A_{min}})^2}{kT}=e^{-\frac{L^v}{kT}}. \quad (19)$$

(6) Lennard-Jones and Devonshire, *Proc. Roy. Soc.*, **A 163**, 59 (1937).

Table 1[7][8][9]

Substance	Temperature in °C.	F^0 in dyn./cm.	A	A_{min}	A_f	U	U^*	Literature
			in A.^{2}			in 10^{-14} erg/molecule		
Myristic acid	7.2	0.130	46.3	43.0	0.78	28.2		
	9.1	0.149	47.5	40.8	1.08	26.3		
	14.1	0.199	51.0	35.0	6.86	18.4	18	(2) (7)
	17.0	0.228	51.6	33.2	6.97	17.9		
	18.0	0.238	51.8	32.2	9.36	16.7		
	22.3	0.281	52.5	30.5	9.98	16.0		
Pentadecylic acid	17.9	0.142	43.8	41.4	0.032	41.4	61	(2) (9)
α-Bromo C_{17} acid	13	0.013	46.5	36.0	2.07	33.7		(7)
α-Monomyristin	12.5	0.017	70.0	41.5	12.0	16.7		(8)

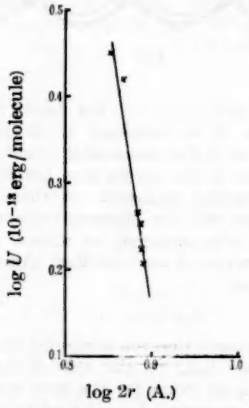

Fig. 2.—Relation between potential energy and intermolecular distance for myristic acid. The straight line is expressed by formula (20).

Unfortunately, the suitable experimental data for the comparison with this estimation are sparse. The values thus estimated of some substances, on which the reliable experimental data are available, are listed in Table 1 with the related matter. The surface vapour pressure of fatty acid, F^0 at definite temperature, in the Table was calculated from the experimental data at the room temperature by assuming that dF^0/dT is 0.01 dyn./cm.,[2] and U^* in the Table is the value of U obtained by Adam and Jessop at about 14°C. with aid of Clapeyron-Clausius' equation.[2] The agreement with both values of myristic acid is satisfactory. On the contrary, the disagreement with the data of pentadecylic acid may be caused from the combination of data of different authors.

If $\log U$ for myristic acid is plotted against $\log 2r$ as shown in Fig. 2 in order to obtain the relation between the potential energy and the intermolecular distance, these points lie nearly on a straight line expressed by the formula

$$U = \frac{3.8 \times 10^{-8}}{(2r)^6} \text{ erg/molecule}, \qquad (20)$$

where r is in A. unit. The most reliable data at the room temperature, is taken as standard. In this case we assume implicitly that U is independent of temperature. If this assumption is justified it may be concluded from (20) that the energy of cohesion in the liquid expanded film is mainly due to van der Waals' force. However, the Harkins' data on the myristic acid[8] are not so regular. We must, of course, remember that all the data cited here were measured on the acidulated substrate, so that the dissociation was repressed. The deviation from the line shown in Fig. 2 may be corrected by the exact measurement of the surface vapour pressure.

In conclusion, although the theory contains some assumption, it is sure that a new measure has been presented for the surface phenomena, and that the problems proposed here may be brought to a settlement only by the exact and systematic experiment. Nevertheless, if the adequate data for the homologous series can be obtained, it may be possible to describe the interaction between the molecules in the liquid film.

The author wishes to express his sincere thanks to Prof. T. Isemura for his kind advice and encouragement.

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(7) N. K. Adam and G. Jessop, *Proc. Roy. Soc.*, **A 112**, 862 (1926).
(8) N. K. Adam and G. Jessop, Ibid., **A 117**, 532 (1927).
(9) G. C. Nutting and W. D. Harkins, *J. Am. Chem. Soc.*, **61**, 2040 (1939).

On a Relation between Dielectric Constant and Heat of Vaporization of Non-polar Liquids.

By Akiyoshi WADA

(Received May 6, 1952)

The nature of the attractive force between two molecules with no permanent electric moment was first explained by London[1] as a "dispersion force". As is well known, it is due to the polarization of each molecule by the other. Even though each molecule is centro-symmetrical, that is, a non-polar molecule, it always has some instantaneous dipole moment caused by the internal electronic oscillation. Such an instantaneous dipole moment of each molecule polarizes the other and produces an attractive force.

On the other hand, according to Onsager[2], if an electric dipole μ is immersed in a dielectric, whose dielectric constant, ε, is larger than 1, it is stabilized by the amount ΔE:

$$\Delta E=\frac{(\varepsilon-1)}{2\varepsilon+1}\cdot\frac{\mu^2}{a^3}\cdot N, \qquad (1)$$

where a is the radius of the molecule, and N is Avogadro's number.

Now if we take ε of Eq. (1) equal to the dielectric constant of the non-polar liquid and μ its instantaneous dipole moment, then the energy of vaporization, E_{vap}, is approximately equal to the mean energy of the ΔE given by Eq. (1);

$$E_{vap}=\frac{(\varepsilon-1)}{2\varepsilon+1}\cdot\frac{\overline{\mu^2}}{a^3}\cdot N. \qquad (2)$$

The effective dipole moment of the molecule is estimated as follows: The "dispersion energy" between two molecules separated by distance R is

$$-\frac{3}{4}\cdot\frac{I_0\alpha^2}{R^6}, \qquad (3)$$

where α is polarizability and I_0 is the ionization potential of the molecule. While the energy of interaction between polarizability α and the mean dipole moment $\overline{\mu^2}$ is

$$-\frac{2\overline{\mu^2}\alpha}{R^6}. \qquad (4)$$

By equating Eqs. (3) and (4), we have

$$\overline{\mu^2}=\frac{3I_0\alpha}{8}. \qquad (5)$$

Following Onsager, if the molecule is regarded as a sphere of radius a with a polarizability α, the dielectric constant ε is expressed by the Lorenz-Lorentz formula in the case of non-polar liquid;

$$\alpha=\frac{\varepsilon-1}{\varepsilon+2}\cdot a^3. \qquad (6)$$

Using Eqs. (2), (5) and (6), we obtain the final relation between the heat of vaporization H_{vap} and the dielectric constant:

$$H_{vap}=E_{vap}+RT=\frac{(\varepsilon-1)^2}{(2\varepsilon+1)(\varepsilon+2)}\cdot\frac{3NI_0}{8}+RT. \qquad (7)$$

This equation provides the temperature dependence of heat of vaporization in terms of the dielectric constant at each temperature.

The ionization potential I_0 can be given by the spectroscopic data, but unfortunately we have no such accurate data extending over the all ranges of frequency, so that it shall now be treated as an empirical parameter.

Table 1

	t°C.	H_{vap}(calc.) kcal./mol.	H_{vap}(obs.) kcal./mol.
Benzene	20	8.08	8.11
	60	7.60	7.61
	100	7.08	7.08
	140	6.59	6.46
	180	6.04	5.80
Carbon bisulphide	0	6.80	6.82
	20	6.67	6.67
	46	6.41	6.41

In Table 1, the heat of vaporization H_{vap}(calc.) of benzene and carbon bisulphide calculated by Eq. (7) is compared with the observed values. The experimental data of ε and H_{vap} are taken from the "International Critical Tables". The parameter I_0 is assumed as 12.4 eV. and 8.0e V. respectively, and these figures seem reasonable for these molecules compared with observed values 6.0 eV. and 9.6 eV.[3] in the case of benzene. It will be seen that the temperature dependence of the heat of vaporization is well expressed by this relation.

The writer wishes to express his sincere thanks to Professor Yonezo Morino for his kind advice.

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(1) F. London, *Z. Physik.* **63**, 245 (1930).
(2) L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
(3) P. E. Boucher, *Phys. Rev.* **19**, 189 (1922). "Int. Crit. Table," Vol. 6, P. 72.

On the Molecular Structures of synthetic Estrogens. I. On *meso*-Hexestrol Dimethyl Ether and *trans* $\alpha\alpha'$-Bis (methylthio) stilbene

By Wataru SUETAKA

(Received March 18, 1952)

Since several years ago a certain number of synthetic estrogens have been prepared, and a hypothesis on the reason of their efficacy was presented: they are effective because their molecular structures are closely similar to those of natural ones[1]. In order to discuss the molecular structures of synthetic estrogens, the dipole moment of two substances, *meso*-hexestrol dimethyl ether and *trans* $\alpha\alpha'$-bis (methylthio)-stilbene, were measured. The former is an estrogenic diphenylethane, and the latter probably has the same molecular structure as that of *pp'*-dimethoxy *trans* $\alpha\alpha'$-bis (methylthio) stilbene, an estrogenic stilbene, because these two substances were prepared by the same reaction.

Experimental Part

The density d and the dielectric constant ε of the solutions in benzene or in carbon tetrachloride were measured with pycnometre and a heterodyne beat apparatus. The apparatus and the method used here were already reported elsewhere[2]. The wavelength used is about 150 metres.

The molar polarization P_2 of the solute was calculated by the following equation:

$$P_2 = M_2\{(p_{12}-p_1)/w+p_1\},$$

where

p_{12}: the specific polarization of the solution
p_1: the specific polarization of the solvent
w: the weight fraction of the solute
M_2: the molecular weight of the solute

If $P_{2\infty}$ designates P_2 at the infinite dilution, the dipole moment at the temperature T is calculated by the equation

$$\mu = 0.0127\sqrt{\{P_{2\infty}-(P_E+P_A)\}T} \quad \text{(in Debye unit)}$$

where

P_E: the electronic polarization of the compound
P_A: the atomic polarization of the compound

P_E was taken to be equal to the molar refraction MR_D for D sodium line, which was calculated by atomic refraction given in "Landolt-Börnstein Tabellen", and P_A was assumed to be 5% of MR_D. The solution, with which the experiment was carried out, were so dilute, that $P_{2\infty}$ was safely taken to be equal to the mean value of P_2's.

The solvent benzene was made free from thiophene by aluminium chloride. It was then dried over metallic sodium and distilled; the fraction boiled within 0.5°C. was collected for use. Carbon tetrachloride is the highest commercial grade, which was distilled, dried over calcium chloride and redistilled; the fraction boiled within 0.3°C. was collected for use. One of the samples *trans* $\alpha\alpha'$-bis (methylthio) stilbene, was kindly prepared by Dr. R. Ikeda of the Chemical Laboratory, Faculty of Science, Tokyo University and the other was prepared by Teikoku Zoki Co. Their purity was confirmed by the measurement of melting points: m. p. 143.9—144.0°C. for *meso*-hexestrol dimethyl ether, and 146.5—148.0°C. for *trans* $\alpha\alpha'$-bis (methylthio)-stilbene.

The results of the measurements are given in Table 1, 2 and 3.

Table 1

The Dielectric Constants and the Densities of *meso*-Hexestrol Dimethyl Ether in Carbon Tetrachloride Solutions at 25°C.

w	ε	d (g./cc.)	P_2 (cc.)
0.00000	2.2260	1.58329	—
0.00629	2.2421	1.57907	158.6
0.01098	2.2529	1.57360	162.8
0.01606	2.2632	1.56901	159.1

$P_{2\infty} = 160.2$ cc. $\quad \mu = 1.77$ (D)

Table 2

The Dielectric Constants and the Densities of *meso*-Hexestrol Dimethyl Ether in Benzene Solutions at 25°C.

w	ε	d (g./cc.)	P_2 (cc.)
0.00000	2.2720	0.87236	—
0.01374	2.2861	0.87408	145.0
0.03509	2.3109	0.87736	146.6

$P_{2\infty} = 145.8$ cc. $\quad \mu = 1.57$ (D)

(1) E. C. Dodds, L. Goldberg, W. Lawson and R. Robinson: *Nature*, **141**, 248 (1938).
(2) S. Mizushima, Y. Morino and K. Higasi: *Sci. Papers Inst. Phys-Chem. Res. (Tokyo)*, **25**, 159 (1934).

Table 3

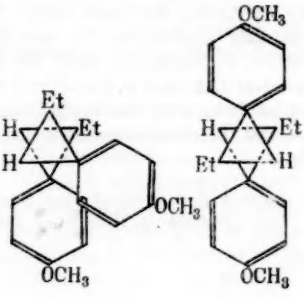
The Dielectric Constants and the Densities of *trans* αα'-Bis (methylthio) stilbene in Benzene Solutions at 30°C.

w	ε	d (g./cc.)	P_2 (cc.)
0.00000	2.2620	0.86610	--
0.01172	2.2741	0.86908	120.0
0.01531	2.2774	0.86990	118.9

$P_{2\infty} = 119.5$ cc. $\mu = 1.24$ (D)

Discussion of the Result

1. *meso*-Hexestrol Dimethyl Ether—As this compound has a C—C rotational axis in its center, two isomers may exist in principle with regard to this axis, the one being the trans form, and the other the gauche form, as shown in Fig. 1.



cis $\mu = 2.06$ D *trans* $\mu = 1.75$ D

Fig. 1.

The dipole moments of two isomers were estimated by vector addition. For the moment of CH_3—O bond the value 1.29 D estimated from the dipole moment of hydroquinone dimethyl ether 1.70 D[3] under the assumption of the value of 111°[4] for the C—O—C bond angle was used, and for the moment of C—O bond the value 0.78 D* estimated from the dipole moment of anisole 1.35 D[3] under the same assumption. It is assumed that the methyl group makes free rotation about C—O axis. For both the moments of H—C and C_2H_5—C bonds, the value of 0.3 D was assumed. The resultant moment of the *trans* and the *gauche* form thus computed are 1.75 D and 2.06 D respectively.

On comparing them with the observed moments, the value 1.77D* observed in carbon tetrachloride solution is almost equal to that of the *trans* form. Hence it may be concluded that, if ever exist, there is only small amount of the *gauche* form in carbon tetrachloride solution. This conclusion may be justified, when taking into account the fact that in the *gauche* form two *p*-methoxyphenyl groups and two ethyl groups come mutually too near to make this form stable. The fact that this compound is of the *trans* form makes it favourable that this compound has the molecular structure similar to that of natural estrogen. The observed moment in benzene solution 1.57 D is lower than that in carbon tetrachloride solution. But the interpretation of this result seems to be difficult.

2. αα'-Bis (methylthio) stilbene—This compound has two isomers: the *trans* and the *cis* isomers with regard to the central C=C bond. The isomer used for the measurement was obtained as crystal and the other isomer remained in the solution as oil. Since these *trans* isomers generally have higher melting points than that of the *cis* isomers, the isomer used for the measurement seems to be the *trans* one. The determination whether this compound has *trans* or *cis* form is also an object of this research.

If this compound has a structure closely similar to that of natural estrogen, it must have the configuration as shown in Fig. 2.

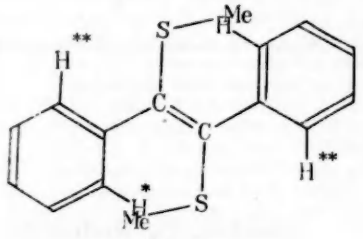


Fig. 2.

This configuration has a center of symmetry and hence has a dipole moment equal to zero. The experimental value, however, does not satisfy this expectation, so evidently this compound is not fixed in this configuration. Then the decision of the structure of this compound is interesting. At first sight it might be considered that the benzene planes are fixed on the same plane as that of the four bonds neibouring to the C=C bond by the quantum mechanical resonance between the phenyl groups and central C=C bond. But if the benzene rings are fixed on this plane, the distances between the methyl groups and the H* or H** atoms attatched to the phenyl groups at the *ortho*-positions must be shorter than 2.7 A. This distance is definitely shorter than 3.2 A., the sum of the van der Waals' radii, therefore probably the benzene rings are twisted from the plane. This conjecture agrees with the result of the ultraviolet absorption spectra of the similar compounds. The resultant moment of this molecule depends on the relative positions of the two methyl

* For this value, from the dipole moment of phenyl ether 1.35D, [5] 0.89D is estimated under the same assumption.

(3) S. Mizushima, Y. Morino, and H. Okazaki: *Sci. Papers Inst. Phys-Chem. Res. (Tokyo)*, **34**, 1147 (1943).

(4) R. Maxwell: *J. Opt. Soc. Am.*, **30**, 374 (1940).

(5) L. G. Groves and S. Sugden: *J. Chem. Soc.*, **1937** 1782.

groups, which can rotate around the S—C bond. Using the moment 1.15 D for CH_3—S bond, which has been obtained from the moment 1.40 D[6] of dimethyl sulphide and the C—S—C bond angle 105°[4], the observed value 1.24 D of this compound provides the value 112° of angle between the two S—CH_3 bonds. If both of the S—CH_3 bonds rotate in reverse directions, starting from the *trans* position as shown in Fig. 2, the positions of rotational angles 34°, 146°, and a pair of 60° and 222°, give the observed moment. Of these positions only that of the rotational angle 34° is favourable for this compound to maintain the molecular structure similar to that of natural estrogen. Assuming the values of C—C: 1.54 A., C=C: 1.34 A., C—S: 1.82 A., C—H: 1.07 A., <C=C—C: 120° and <C—S—CH_3: 105°, when the rotation by 34° around the S—C bond is assumed, the benzene rings must be twisted circa 75° from the plane, in order to keep the H* atom at the distance 3.2 A. from the methyl groups. This structure has the distances 3.12 A. between CH_3 groups and H** atoms, but the distances among the groups in a molecule generally can be shorter than the van der Waals' distances, thus probably this structure is realized.

In this place it is worth while to compute the moment of the *cis* isomer. The *cis* isomer has also the axes of rotation around S—C bonds. Assuming the moment 0.85 D for C—S bond, 1.15 D for CH_3—S bond, and 0.3 D for H—C bond, the simple vector addition gives the value from 0.40 D to 3.12 D for the moment of the *cis* isomer. But if the configurations are excluded, in which the distance between the two methyl groups is within 4.0 A., the sum of the van der Waals radii, the structure having the moment smaller than 1.30 D are not allowed to exist. The observed value 1.24 D lies in this unallowed region. Thus it might be concluded that this compound is not the *cis* isomer. But taking into account the basic assumtion for this calculation, it seems unreasonable to insist only from this reason that this compound is the *trans* isomer.

From the discussion described above it seems that these substances have general resemblance to natural estrogen in their molecular structures.

I wish to express my deep gratitude to Prof. Y. Morino and Dr. I. Miyagawa of the Chemical Laboratory, Faculty of Science, University of Tokyo, for their many helpfull suggestions and discussions. I am also indebted to Dr. T. Takahashi and Dr. M. Ōki of the Chemical Laboratory, Faculty of Science, University of Tokyo, for their kind supply of the sample and their encouragement throughout this work.

Research Laboratory of Fuel Science, Tokyo Institute of Technology, Tokyo.

(6) H. Staude "Physikalisch-chemisches Taschenbuch" (1945).

Electrolytic Reduction of Aromatic Carboxylic Acids. I. Reduction of Benzoic Acid under Pressure[1]

By Shin-ichi Ono and Tsuneo Yamauchi

(Received May 7, 1952)

A number of investigations have been carried out on the electrolytic reduction of benzoic acid, but all of them were made at ordinary pressure in an open vessel. The authors, therefore, studied this problem under the pressure of hydrogen and carbon dioxide to find out the effect of the pressure on the reduction products.

(1) Reduction of Benzoic Acid to Benzylalcohol.—C. Mettler[2], Fr. Fichter and Israel Stein,[3] H. Inoue,[4] Sherlock Swann and G. D. Lucker,[5] studied this problem in the alcoholic sulfuric acid solution by using a lead cathode with good yields. The authors carried out electrolysis in alcoholic sulfuric acid solution by using a lead cathode and compared the yield of benzyl-alcohol obtained under the various pressures of hydrogen and carbon dioxide with that obtained in an open

(1) Presented at the annual meeting of the Chem. Soc. of Japan in 1950.

(2) C. Mettler, *Ber.*, **38**, 1745 (1905).

(3) Fr. Fichter, Israel Stein, *Helv. Chim. Acta.*, **12**, 821 (1929).

(4) H. Inoue, *J. Soc. Chem. Ind. Japan*, **24**, 806 (1921).

(5) Sherlock Swann and G. D. Lucker, *Trans. Electrochem. Soc.*, **75**, 411 (1939).

vessel. Not only hydrogen but also carbon dioxide had an important effect on the yield of the reduction product. The yield increased in proportion to the pressures of hydrogen or carbon dioxide respectively. (Table 1)

(2) Reduction of Benzoic Acid to Benzaldehyde. — Hugo Weil[6] and Mettler[7] studied this problem by using a mercury cathode and benzene, and obtained benzaldehyde with 30—50% yield. Benzaldehyde was removed to a benzene layer from a water layer and protected from reduction to alcohol.

S. Tesh. Alexander Low[8] obtained 50% benzaldehyde by using sodium bisulfite which combined with benzaldehyde instead of benzene, but only 20% by Mettler's method.

The authors carried out the electrolysis by using a mercury cathode in a mixture of boric acid, sodium sulfate solution and benzene. The yield increased in accordance with the pressure of hydrogen. In case of carbon dioxide the yield decreased as the pressure increased. (Table 2)

(3) Reduction of Benzoic Acid to Ethyl Hexahydrobenzoate.—Emill Müller[9] electrolysed benzoic acid in alcoholic sulfuric acid solution by using a lead cathode, and obtained a hydro-compound, but F. Somlb[10] identified this to be dihydro benzoic acid ethylester. Fr. Fichter[11] obtained benzylalcohol mainly by the same method, and predicted that one will obtain hydro-compound when the current density is small.

The authors carried out the electrolysis in alcoholic sulfuric acid solution by using a platinized platinum cathode. When the pressure of hydrogen or carbon dioxide was increased, the yield of ethylhexahydrobenzoate decreased but the yield of hexahydrobenzoic acid increased.

It was thought that ethyl benzoate was formed from benzoic acid under this condition and the ester was reduced to ethyl hexahydrobenzoate.

It was found that the electrolytic reduction of benzoic acid at a platinized platinum cathode in alcoholic sulfuric acid solution gave rise to hexahydrobenzoic acid and its ester, but no benzylalcohol.

These results contrast sharply with that obtained from a lead cathode. It was assumed that there would be an essential difference between the nature of lead and platinized platinum cathode in the course of reduction.

Examination of the Table 4 shows that the hydrogen pressure has an effect on the reduction products.

(6) Hugo Weil, D. R. P. 196, 293 (1906).
(7) C. Mettler, *Ber.*, **41**, 4148 (1906).
(8) Alexander Low, *Tran. Am. Elec. Chem. Soc*, **45**, (1924).
(9) E. Baur and E. Müller, *Zeit. Elektrochem.*, **34**, 98 (1928).
(10) F. Somlb, *Zeit. Elektrochem.*, **35**, 264 (1929).
(11) Fr. Fichter, *Helv. Chim, Acta.*, **12**, 821 (1929).

Experimental

(1) Reduction of Benzoic acid to Benzylalcohol.—The electrolytic conditions were as follows: cathode: lead plate, 1 dm.^{2}; cathodic solution: 10 g. of benzoic acid, 70 g. of sulfuric acid, 60 g. of ethyl alcohol; anode: lead; anodic solution: 30% sulfuric acid; current density: 5 amp./dm.^{2}; Temperature: 30—50°C.; current quantity: 10 amp. hrs.; Pressure: 1—30 atmosphere.

The temperature was kept under 50°C. by using a water bath and by stirring the cathodic solution vigorously; the current was passed until 10 amp. hrs. were reached.

When the electrolytic reduction was completed, the catholyte was poured into water and extracted with ether. The ether solution was dried with anhydrous sodium sulphate. After the vapourization of the ether, the pale yellow fragrant oil was fractionated at 180—220°C. The fraction was saponified with 2N caustic soda and was extracted with ether and distilled. The fraction between 196—203°C. has specific gravity of 1.045 at 20°C. and refractive index $n_D^{25}=1.5283$ (those of benzylalcohol are $D^{15}=1.0507$, $n_D^{25}=1.53866$ respectively). It dissolved calcium chloride and gave the odour of benzaldehyde when warmed with nitric acid. Thus we regarded this fraction as benzylalcohol. When the residual water solution at the above mentioned extraction was acidified by adding sulfuric acid, the precipitation was gained. This was identified as benzoic acid, judging from its freezing point. Hydrobenzoin and benzene were not detected.

To study the effect of pressure, the electrolytic cell with a stirrer was placed in an autoclave specially designed* for this purpose. The gas was introduced to remove the air, and then the desired pressure was maintained and a series of electrolytic reductions was made under pressures of 1—30 atmosphere.

Result are summerized in Table 1.

Table 1

Pressure of H_2	Yield		Current Efficiency
1 atm.	4.5 g.	50.8%	44.6%
10	5.6	63.2	55.4
15	6.5	73.4	64.4
30	7.2	81.3	71.4
Pressure of CO_2	Yield		Current Efficiency
1 atm.	4.5 g.	50.8%	44.6%
10	5.0	56.4	49.5
20	5.2	58.7	51.5
30	5.5	62.1	54.5

* S. Ono, *J. Chem. Soc. Japan*, **73**, 852 (1952).

(2) Reduction of Benzoic Acid to Benzaldehyde.—The electrolytic conditions were as follows: cathode: mercury (16.2 cm.^{2}); cathodic solution: 6.5 g. of sodium sulphate, 6.5 g. of boric acid, and 5 g. of sodium benzoate were dissolved into 85 cc. of water and 50 cc. of benzene for fixation of the aldehyde added to this solution.

anode: lead; anodic solution: 10% aquous solution of sodium sulphate; current density: 6 amp./dm.^{2}; current quantity: 4 amp. hrs.; temperature: 20—25°C.; presure: 1—30 atm.

After breaking the current, we continued the stirring further on for about one hour to utilize the reducing power of sodium amalgam. Then the catholyte was separated from mercury and 100 cc. of 10% sulfuric acid was added and steamdistilled. The distillate was extracted with ether and the ether solution was neutralized with sodium bicarbonate to remove the unreduced benzoic acid to the water layer.

The ether solution was dried with anhydrous sodium sulphate. After stripping the ether, we gained benzaldehyde with boiling point 179°C. The water solution was acidified and the precipitated benzoic acid was recovered. On the contrary, aldehyde was not obtained in the case of lead-, platinized platinum-, or copper-cathode. This reason is explained as follows: Mercury acts as sodium amalgam by which benzoic acid is reduced to aldehyde, and then sodium amalgam turns back to mercury. In this case, the system of the mercury and sodium amalgam was circulated by electrolysis. Thus the yield of aldehyde was increased by keeping the experimental conditions to suit the formation of sodium amalgam. If the catholyte became alkaline, the velocity of the action of sodium amalgam on benzoic acid was slowed down. On the contrary, by maintaining it in a condition to make the above-said velocity speedy, the formation of sodium amalgam was decreased.

When the electrolytic reduction was undertaken at high pressure of hydrogen atmosphere, the yield of aldehyde was increased with the pressure, but in the carbon dioxide atmosphere the yield was decreased with the increase of the pressure. The latter can be illustrated as follows: the increase of the amount of carbon dioxide dissolved in catholyte decomposes sodium benzoate to benzoic acid and the catholyte increases acidity, so that the yield decreases. It seems that the dissolution of carbondioxide and benzoic acid in benzene makes the dissolution of aldehyde in benzene more difficult.

Results are summarized in Table 2.

Table 2

Pressure of H_2	Yield		Current Efficiency
1 atm.	0.6 g.	16.3%	7.6%
20	1.1	29.9	13.9
30	1.6	43.3	20.1
Pressure of CO_2	**Yield**		**Current Efficiency**
1 atm.	0.6 g.	16.3%	7.6%
10	0.3	8.2	3.8
20	trace	—	—

(3) Reduction of Benzoic Acid to Ethyl Hexahydrobenzoate.—The electrolytic conditions were as follows: cathode: platinized platinum (84.2 cm.^{2}); cathodic solution: 10 g. of benzoic acid, 120 cc. of 95% alcohol, 30 g. of sulfuric acid; anode: lead; anodic solution: 30% sulfuric acid; current density: 0.5—1.0 amp./dm.^{2}; temperature: 20—30°C.; current quantity: 15—20 amp. hrs.; pressure: 1—30 atm. After electrolysis, the catholyte was filtered and the greater part of solvent was taken off under reduced pressure. The results of fractional distillation of 20 g. products are shown in Table 3.

Table 3

	fraction	yield	D_4^{25}	n_D^{25}
(1)	185—195°	5 g. (25%)	0.9506	1.4373
(2)	195—200°	9 (45)	0.9525	1.4396
(3)	200—225°	4 (20)	1.0500	1.4525
(4)	225—240°	1.6 (8)	—	—

The fraction (2) which is a colorless liquid ought to be ethyl hexahydrobenzoate from its physical constant and the hydrolysis of the fraction (2) produced hexahydrobenzoic acid. The fraction (3) seemed to be the mixture of hexahydrobenzoic acid and its ethyl ester from its physical constant. Saponification of (3) with 20% alcoholic potassium hydroxide, gave a hexahydrobenzoic acid, M. P. 28°C. The fraction (4) a greater portion of which was distilled at 233—237°C., seemed to be hexahydrobenzoic acid, but we could not confirm it as its amount was too small.

The relation between the amounts of four fractions and the pressure is shown in Table 4.

Table 4

Press. atm. / Fraction	1 (H_2)	5 (H_2)	10 (H_2)	30 (H_2)	10 (CO_2)	20 (CO_2)
(1) 185—195°	25%	25%	20%	23%	30%	25%
(2) 195—200°	45	40	35	23	30	25
(3) 200—225°	20	20	28	35	25	30
(4) 225—240°	8	10	12	17	10	15

In the case of the electrolytic reduction under pressure, the fraction (2), that is the ethyl hexahydrobenzoate was decreased and the fraction (3) (4) that is the mixture of ethyl hexahydrobenzoate and its acid was increased with the increase of the pressure of hydrogen. When ethyl benzoate is catalytically reduced, either hexahydro-compound or benzyl alcohol is obtained according to the catalyst. In the case of the electrolytic reduction of benzoic acid (benzoic ester) using a platinized-platinum cathode, the authors obtained ethyl hexahydrobenzoate and its acid but no benzylalcohol with small current density at ordinary or high pressures. But the yields of the reduction products differ according to the pressure.

Summary

The authors studied the electrolytic reduction of benzoic acid and compared the yield of the reduction product obtained under various pressures of hydrogen and carbon dioxide with that obtained in an open vessel. The effect of pressure in the course of electrolytic reduction was discussed and it was found that the reduction product differed according to the pressure.

The authors express their gratitude to Dr. N. Sugiyama, Professor of the Tokyo University of Education and Dr. B. Sakurai, professor of the Shinshu University for their kind advice. The expense of this work has been defrayed from the Grant in Aid for Scientific Research from the Ministry of Education, to which the authors' thanks are due.

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Fractionation of Cellulose Acetate and Distribution of Non-Cellulosic Components between the Fractions

By Kei MATSUZAKI, Setsuo FUKUHARA, Akira HATANO and Hiroshi SOBUE

(Received May 14, 1952)

Introduction

As raw materials for the production of cellulose acetate, cotton linters have usually been used, but recently wood pulps purified more than 95% α have been used, mixed with or without cotton linters. Also in Japan, studies of high-grade pulp for cellulose ester are now in progress.

It has generally been observed[1] that acetone solutions of cellulose acetates from wood pulp are hazy, and films and fibers produced are weaker in strength than those from cotton linters. It is important and interesting to make clear the cause of these defects of wood pulp although the haziness of the solution does not prevent their application to fibers.

In this research, secondary cellulose acetates from linters and pulp were fractionated and their chain-length distributions were compared, and viscosities in acetone and cupriethylene diamine solutions, acetic acid contents and pentosan contents of the individual fractions were determined.

Much[2] has been written about fractionation of secondary cellulose acetate but only recent investigations will be referred to here. Sookne et al.[3] fractionated cellulose acetate by precipitation with ethanol from acetone solution and obtained fifteen fractions. The acetic acid content remained constant for all fractions except three of very low chain length which showed slightly higher values. Most of the haze-producing material in the acetate was found to be contained in the higher-molecular fraction. But details of the experiment are not known in Japan. Howlett and Urquhart[4] fractionally dissolved acetate and found that the high-molecular fraction, which was low in acetic acid content, gave a hazy acetone solution. Scherer and Thompson[5] used the acetone-water-heptane system and D. P. of the first fraction was lower than that of the second. The acetic acid content of the fractions increased from 51.1 to 54.9% as the D. P. decreased on account of acetolysis. Wales and Swanson[6] believed the incomplete solubility of the first fraction to be dsua c by association between calcium ions and sulfuric half-ester groups or carboxyl groups of the polymer. Any further study of the incompletely soluble fraction has not yet been made.

(1) C. J. Malm, *Svensk Papperstidn.*, **50**, Häggiund Issue 135 (1947).

(2) L. H. Cragg and H. Hammerschlag, *Chem. Rev.*, **39**, 79 (1946).

(3) A. M. Sookne, H. A. Rutherford, H. Mark and M. Harris, *J. Res. Nat. Bur. Standards*, **29**, 123 (1942).

(4) F. Howlett and A. R. Urquhart, *J. Textile Institute*, **37**, T89 (1946).

(5) P. C. Scherer and R. B. Thompson, *Rayon & Synthetic Textiles*, **32**, No. 9, 69; No. 10, 51 (1951).

(6) M. Wales and D. L. Swanson, *J. Phys. & Colloid Chem.* **55**, 203 (1951).

Experimental Procedures and Results

The samples used were cellulose acetates from cotton linters, Rayaceta and a domestic pulp. The samles (each 5 g.) were dissolved in acetone to give 1% solution and fractionally precipitated with ethanol. The precipitant was added to give a slight precipitate in the solution, then the solution was warmed in a water bath to make it clear and kept standing in an incubator for 24 hours. The precipitate formed was separated from the supernatant liquid, washed with water and dried in a vacuum desiccator. The last fraction was obtained by evaporating and concentrating the solution and by filtering the precipitate on a glass filter. The D. P. calculated from the viscosity of acetone solution and the pentosan content of each fraction were tabulated in Tables 1—3. (in acetone $Km=9\times10^{-4}$ at 20°C.). The acetic acid content of each fraction was also determined. Fractions incompletely soluble in acetone showed slightly lower acetic acid content but the result was not clear as the accuracy of the determination was low, on account of the small quantity of the sample (0.1 g.). Then 20 g. of another acetate from Rayaceta was fractionated into five fractions and the D. P. from acetone solution, the D. P. from cupriethylene diamine solution, the acetic acid content and the pentosan content of each fraction were determined. The results are shown in Table 4. In this case, the first fraction was divided into two fractions by redissolving in acetone, the upper hazy solution (F1S) and the under gel-like precipitate (F1P).

Table 1

Fractionation of Cellulose Acetate from Cotton Linters. AcOH 54.7%, D. P. 200, Pentosan under 0.02%

Fraction	Weight %	D. P.	Solubility in Acetone	Pentosan %
1	0.60	400	81.7	—
2	6.72	352	hazy	0.07
3	8.72	290	100	<0.02
4	9.30	276	100	<0.02
5	9.97	255	100	<0.02
6	8.88	224	100	<0.02
7	11.50	189	100	<0.02
8	3.68	184	100	<0.02
9	4.57	158	100	<0.02
10	4.70	140	100	<0.02
11	4.22	126	100	<0.02
12	6.98	111	100	<0.02
13	5.63	103	100	<0.02
14	15.16	59	hazy	0.04

Table 2

Fractionation of Cellulose Acetate from Rayaceta. AcOH 54.7%, D. P. 210, Pentosan 0.1%

Fraction	Weight %	D. P.	Solubility in Acetone	Pentosan %
1	0.20	—	—	—
2	3.63	260	85.3	0.5
3	4.25	300	26.9	1.0
4	3.58	353	92.4	0.25
5	5.11	396	100	<0.02
6	2.23	340	100	<0.02
7	14.50	308	100	<0.02
8	7.39	267	100	<0.02
9	6.23	233	100	<0.02
10	4.81	205	100	<0.02
11	7.35	189	100	<0.02
12	8.57	162	100	<0.02
13	5.35	131	100	<0.02
14	3.15	118	100	<0.02
15	9.87	101	100	<0.02
16	6.17	63	100	<0.02
17	7.58	35	yellowish hazy	0.1

Table 3

Fractionation of Cellulose Acetate from a Domestic Pulp. AcOH 55.7%, D. P. 261, Pentosan 0.3%

Fraction	Weight %	D. P.	Solubility in Acetone	Pentosan %
1	10.79	260	precipitate, soly. not determined	1.0
2	8.37	429	precipitate, soly. not determined	1.5
3	5.79	440	hazy	0.2
4	5.22	411	100	<0.02
5	8.95	342	100	<0.02
6	10.49	316	100	<0.02
7	5.39	277	100	<0.02
8	4.75	245	100	<0.02
9	8.71	197	100	<0.02
10	4.90	170	100	<0.02
11	5.78	147	100	<0.02
12	5.34	116	100	<0.02
13	4.23	83	100	<0.02
14	6.13	66	100	<0.02
15	5.16	35	82	0.1

Table 4

Fractionation of Cellulose Acetate from Rayaceta

Fraction	Weight %	D. P. in Acetone*	D. P. in Cu(En)$_2$**	Solubility in Acetone	AcOH %	Pentosan %
original	—	165	163	100	54.8	0.1
1S	8.52	217	203	hazy	54.8	0.3
1P	3.25	184	176	58	—	0.7
2	33.79	227	227	100	54.8	<0.02
3	17.36	162	163	100	54.6	<0.02
4	16.22	107	133	100	54.8	<0.02
5	20.86	66	68	100	55.0	0.03

* $Km=9.0\times10^{-4}$ for cellulose acetate at 20°C.
** $Km=8.8\times10^{-4}$ for cellulose at 20°C.

Discussion

From Tables 1—3, it is seen that the acetate from linters gives only 0.60% of the first incompletely soluble fraction and inversion of D. P. is not observed when solubility of the fraction is taken into consideration, whereas, in the case of the acetate from Rayaceta, the fractions from the first to the fourth are incompletely soluble in acetone and considerable inversion of viscosity is observed even when solubility of the fractions is considered. Scherer and Thompson[5] thought that this was due to the migration of the low-molecular portion into the acetone-insoluble fraction. But we believe this is not the case. It seems these fractions may have actually a low D. P..

In Table 4, the D. P.s of both F1S and F1P are lower than that of F2. We could not decide whether this was due to the presence of the haziness which would prevent the accurate determination of the concentration of the solution, or due to associated products in the solution. If the former is true the D. P. determined from the viscosity of the completely dissolved solution of the fraction would be higher. Therefore viscosity in cuprietlylene diamine solution was determined.

Cellulose acetates are saponified and dissolved in cuprietlylene diamine solution. Unesterified cellulose and esterified pentosan would be also dissolved and associated products would dissociate into molecular dispersion. The determination in diamine solution shows the same results as in acetone. D. P. of F1S is higher than that of F1P. This indicates that a part of F1S is a normal fraction which should have a higher D. P. than that of F2, if separately precipitated from the abnormal fraction in F1S, and have normal molecular shape. Then Scherer's opinion might be wrong. Abnormal materials included mainly in F1P and partly in F1S, having actually a low D. P., are responsible for the inversion of the D. P.

A comparison between chain-length distributions of the acetates from cotton linters and Rayaceta shows that the latter has a rather heterogeneous distribution, although their average D. P.s are almost the same. Our previous investigation,[7] as those of others,[8] showed that the chain-length distribution of a wood pulp is more heterogeneous than that of purified cotton and the heterogeneity does not disappear even if acid-hydrolysis takes place. Both the difference in the heterogeneity of the chain-length distribution of the acetates, which Malm could not prove experimentally, and the heterogeneity in chemical composition e. g. acetone-insoluble fractions, may account for the weakness in their mechanical properties and for their viscometric behavios.

Next, the pentosan content of each fraction was determined. The determination by phloroglucin gives about 1% of pentosan content even to pentosan-free materials such as glucose or linters, on account of oxymethyl furfural produced from hexose. The error due to oxymethyl furfural increases as the pentosan content decreases. A part of the error can be corrected by treating the wet precipitate of the phloroglucide with ethanol,[9] but a trace of pentosan (under 0.1% of the sample) would not be detected and determined. Therefore, determination of pentosan by paperchromatography[10] was adopted.

Tables 1—3 indicate that all fractions which give a hazy acetone solution or show incomplete solubility in acetone, include pentosan. The last fractions obtained by evaporating the solvent also include pentosan, but its quantity is small.

It is noticed that even the acetate from linters include pentosan, though it can not be detected from the acetate itself. It is concentrated in the first, second and the last fraction. The acetate from Rayaceta contains 0.1—1.0% pentosan in its initial fractions and the last fraction. The behavior of the acetate from a domestic pulp was almost the same.

These indicate that there is a clear relationship between pentosan content and the haziness of acetone solution of acetates as Jayme and Schenck[11] proved. It is observed that the greater the pentosan content of a fraction, the greater the haziness of its acetone solution or its acetone-insolubility. The acetates from wood pulp invariably include a higher content of the portions which show incomplete solubility in acetone and a higher content of pentosan. Table 4 shows that F1P contains more pentosan than F1S. The acetic acid content of each fraction remained almost constant. Since the acetic acid content of F1P could not be determined, it is still uncertain that the acetone-insoluble fractions are low-esterified cellulose.

Thus, it can not be decided whether the

(7) K. Matsuzaki and H. Sobue, This Bulletin, **24**, 184 (1951).

(8) L. Jörgensen, Dissertation, Oslo 1950; N. Glarén, Dissertation, Uppsala 1944.

(9) H. Sobue, K. Matsuzaki and T. Abe, unpublished work.

(10) H. Sobue, K. Matsuzaki, A. Hatano and U. Arisawa, *J. Soc. Tex. Cell. Ind. Japan*, **8**, 79 (1952); H. Sobue and A. Hatano, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **55**, 131 (1952).

(11) G. Jayme and U. Schenck, *Melliand Textilberichte*, **31**, 153, 230 (1950).

insoluble fractions are due to association by the salt bridge effect of calcium ions between carboxyl or sulfuric half-ester groups as Wales and Swanson[6] suggested, or due to the remaining structure (e. g. incompletely digested fragments) of the wood tissues which could be considerably acetylated but would not yield a mono-molecularly dispersed solution. In our opinion, both are responsible but the latter more so, because the hazy portions are always accompanied by pentosan, and the determination of the protein content of each fraction by paper chromatography revealed that the acetone insoluble fractions include it more than acetone soluble fractions. But it does not seem that all pentosan is combined with cellulose, a part of it is molecularly dispersed, and acetylated, saponified and precipitated, though most of it is removed in the saponification stage. (e. g. Rayaceta contained 0.5% pentosan, the acetate 0.15% based on cellulose)

Now we may say the following as to the acetylation and refining of wood pulp.

1. Pentosan in pulp must be removed as far as possible although most of it is removed during the ripening stage as above mentioned. Pentosan itself or pentosan-cellulose complex cause haziness of the acetone solution and result in heterogeneity of the acetate. Pentosan remained as an important index for the degree of the refinement of pulp.

2. Carboxyl and sulfuric acid groups must be removed as far as possible. Sulfuric acid groups can be removed in the stabilization process. Carboxyl groups are mainly formed during bleaching stages. In this respect, bleaching which does not accompany modification and degradation of cellulose, such as by sodium chlorite, is prefered.

3. Jayme classified acetylation characteristics of pulp into those inherent to pulp and those produced by pretreatments etc. All the above mentioned are referred to the characteristics inherent to pulp. Of course, pretreatments and drying conditions etc. (e. g. boiling after cold alkali refinement and the drying temperature must not be raised over 60°C. and the drying must not be continued until they become bone-dry) should be controlled strictly.

Experimental

Pentosan content was determined as follows. 0.2—0.3 g. of a sample was dissolved and degraded in 70% sulfuric acid, diluted to 2—3% and boiled under reflux for 8 hours. Saccharide solution refined by the usual method was developed by butanol-water-acetic acid mixture (4:1:1). Quantitative estimation was made by determination of the area of the spot or of the intensity of the light transmitted through the spot colored by aniline hydrogen phthalate. As the spots of glucose and xylose were overlapped slightly, the area method was generally adopted. Amino acid was colored by ninhydrine, and approximate estimation was made by its color intensity.

Cupriethylene diamine solution was prepared after T230 Sm—50.[12] The acetates were dissolved in this solution and kept under nitrogen atmosphere for 24 hours.

Acetic acid content was determined as follows. About 0.5 g. of a sample was dissolved in 50 cc. of acetone, saponified with 50 cc. of 0.2 N potassium hydroxide solution. After three hours, 50 cc. of 0.2 N hydrochloric acid solution was added and back titrated with the alkali.

As the D. P.s were determined in 0.6% solution, the solubilities were also determined in this solution. D. P.s of the incompletely soluble fractions were corrected for the solubilities when they were known. It was observed that the insoluble fractions became gradually dispersed as the concentration of the solutions was lowered. This is seen from the fact that F1P which was at first a gel-like precipitate showed 58% solubility by redissolving in acetone.

Summary

1. Three cellulose acetates from cotton linters, Rayaceta and a domestic pulp were fractionally precipitated from acetone solution with ethanol, and viscosity measurements in acetone solution and pentosan determinations by paper chromatography of the individual fractions were made.

2. Another acetate from Rayaceta was again fractionated into five fractions and viscosities in acetone and cupriethylene diamine solution and pentosan contents of the individual fractions were determined.

3. The results showed a close relationship between the initial acetone-insoluble fractions or in acetone haze-producing fractions and their pentosan content. These fractions include abnormal materials which show low viscosity (probably low D. P.) in cupriethylene diamine solution as well as in acetone. They are included much in the acetates from wood pulps.

4. It could not be decided whether these acetone-insoluble fractions were due to association by salt bridge effect of calcium ions between carboxyl or sulfuric half-ester groups, or due to the remaining structure of wood tissues.

5. The chain-length distributions of the cellulose acetates from wood pulp seem to be more heterogeneous than those from cotton linters.

(12) Tappi Standard.

The authors express thanks to Mr. T. Ueki and Miss K. Saito for their earnest aid to the experiment. The expense of the work was defrayed from the Scientific Research Encouragement Grant of the Department of Education.

Department of Applied Chemistry, Faculty of Engineering, Tokyo University, Tokyo

Vat Dyes of Acenaphthene Series. IV. Condensation of Perylenetetracarboxylic Acid Anhydride with *o*-Phenylenediamine[1]

By Toshio MAKI and Harukichi HASHIMOTO

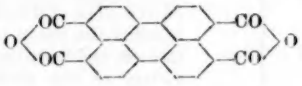
(Received July 5, 1952)

By the condensation of perylenetracarboxylic acid anhydride (I) with aromatic amines scarlet or red vat dyes of N, N'-diaryl-tetracarboxyldiimide type are generally obtained.[2] We have found, however, that the relation is quite particular in the case of *o*-phenylenediamine. At lower condensation temperature (160°) the main product (67.1% of the theory) was N, N'-di (*o*-amino) phenyl-perylenetetracarboxyl-diimide (II), which is soluble in alkaline hydrosulfite and insoluble in 90% sulfuric acid. It dyes cotton in weak, dull-red violet of low value as a vat dye.

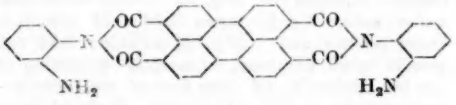
At moderate condensation temperature (190°) a new valuable violet vat dye was obtained as the principal product (60.6%), which is easily soluble in alkaline hydrosulfite and also soluble in 90% sulfuric acid. This dye has a very strong dyeing power and deep violet shade is produced on cotton with 2% dye (1W method). It is really remarkable that this new vat dye has the maximum light fastness (8 grade), highest of all-hitherto known synthetic organic dyes of violet shades. The fastness against chlorine is also maximum. The constitution of this dye is 3, 4-benzimidazole-9, 10-(*o*-amino) phenyl - perylenetetracarboxyl - diimide (III), simply called by us as "Acenaphthene Violet". The remaining amino group is diazotizable.

At the temperatures higher than 200° the main product is 3, 4, 9, 10-perylenetetracarboxyl-bis-benzimidazole (IV), which is a violet blue substance insoluble in alkaline hydrosulfite and for this reason it has no dyeing ability.[3]

As another route N, N'-di (*o*-nitro) phenyl-perylenetetracaboxyl-diimide (V) was prepared by the condensation of perylenetetracarboxylic acid anhydride with *o*-nitroaniline and then



(I)



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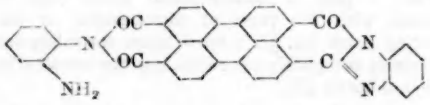
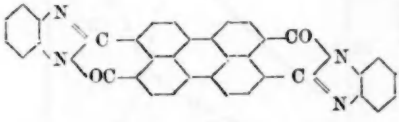
(V)



(III)



(IV)

(1) Read before the 5th Annual Meeting of the Chemical Society of Japan on April 5, 1952.

(2) T. Maki and H. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Section*, **54**, 544 (1951).

(3) G. P. 502352, *Frdl.* **17**, 1393.

reduced with alkaline hydrosulfite containing sodium sulfide at 60°. The diamino compound thus obtained was completely identical with that (II), above mentioned, which had been prepared directly from *o*-phenylenediamine. The effect of thermal treatment on the stability of the three compounds is interesting. Thus, the diamino compound (II) is converted mainly into Acenaphthene Violet (III) by boiling with nitrobenzene for 1~1.5 hours. Acenaphthene Violet can be almost entirely changed into the unvattable bis-imidazole (IV) when boiled with nitrobenzene for 5 hours. The quantitative separation of the three compounds can be carried out using alkaline hydrosulfite and 90% sulfuric acid.

Experimental Part

Condensation of Perlyenetetracarboxylic Acid Anhydride with *o*-Phenylenediamine.—A mixture of 1.96 g. (1/200 mole) of finely powdered perylenetetracarboxylic acid anhydride and 7.5 g. (14/200 mole) of *o*-phenylenediamine was kept in an oil bath without stirring for 4 hours at 190° (bath temperature). In order to remove the excess of *o*-phenylene diamine, 50 cc. of alcohol was added to the product, stirred at 70° for 30 minutes, filtered and washed with alcohol. From this residue the unchanged perylenetetracarboxylic acid anhydride was extracted by heating with 500 cc. of aqueous 1% sodium hydroxide on a water bath, filtering and thoroughly washing with water. Crude condensation product 2.77 g.

Separation.—The crude product was finely powdered, kept with 560 cc. (200 parts) of water, 11 g. (4 parts) of sodium hydroxide and 11 g. (4 parts) of sodium hydrosulfite at 45° for 15 minutes, filtered, and the residue was once more treated with the same amount of the alkaline hydrosulfite solution, filtered, washed with the alkaline hydrosulfite till the filtrate became colorless. The residue was then suspended in 500 cc. of water, acidified with hydrochloric acid, filtered and washed neutral. Yield (IV) is 0.41 g. (15.2% of the theory).

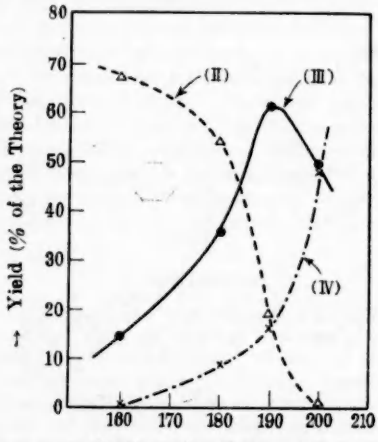


Fig. 1.

The combined violet red filtrate was oxidized by a current of air, the precipitate collected and washed neutral. Yield is 2.27 g. This was then dissolved in 115 g. (50 parts) of 98.7% sulfuric acid, 11.1 cc. of water added dropwise with external ice cooling to produce 90% sulfuric acid and allowed to stand over-night. The precipitate was collected on a glass filter, washed with 90% sulfuric acid, suspended in water and neutralized with sodium carbonate. Yield (II) is 0.55 g. (19.2% of the theory). The 90% sulfuric acid filtrate was poured into 1 l. of ice water, the resulting precipitate collected and washed neutral. Yield (III) is 1.68 g. (60.6% of the theory). The further relations between the condensation temperatures and yields of the three compounds are illustrated in Fig. 1.

3,4-Benzimidazolo-9,10-(*o*-amino)phenylperylenetetracarboxyl-diimide (Acenaphthene Violet) (III).—Black violet powder, insoluble in organic solvents of lower boiling points, sparingly soluble in boiling *o*-dichlorobenzene or nitrobenzene with violet red color and weak red fluorescence. Soluble in conc. sulfuric acid and the solution shows blue (thin layer) and violet blue (thick layer) dichroism with weak red fluorescence. Soluble also in 90% sulfuric acid. Easily soluble in alkaline hydrosulfite and gives violet red vat with weak red fluorescence. Cotton is dyed in deep violet shade with 2% dye (IW method). These cotton dyeings have the maximum fastness against light (8 grade), chlorine (5 grade) and washing (40°—5 grade, 90°—4 grade). Staple fibre is dyed in deep red violet shade even with 1% dye. Found: N, 9.76; Calculated for $C_{36}H_{18}O_2N_4$ (III): N, 10.10%.

When the violet cotton dyeing was diazotized on the fibre and treated with alkaline β-naphthol solution the shade became more red and its light fastness suddenly depressed to 2 grade. By boiling 1.00 g. of the violet dye (III) with 2.0 g. of benzoyl chloride in 20 g. of *o*-dichlorobenzene under reflux for 10 hours 0.54 g. of insoluble violet powder and 0.50 g. of soluble violet red powder were obtained, apparently consisting of the bis-imidazole (IV) (the former) and benzoylated product of (III) (the latter). Both of them were no more vattable with alkaline hydrosulfite. When 1 part of Acenaphthene Violet (III) is heated with 200 parts of nitrobenzene at the boiling point (ca. 211°) for 5 hours the substance is nearly completely converted into the unvattable bis-imidazole (IV).

3,4,9,10-Perylenetetracarboxyl-bis-benzimidazole (IV).—Violet grey powder, insoluble in organic solvents of lower boiling points, sparingly soluble in boiling nitrobenzene giving faint violet red solution with weak red fluorescence. Conc.

sulfuric acid solution is blue without dichroism and fluorescence, from which violet blue precipitate resulted by the addition of water. Insoluble in alkaline hydrosulfite. Found: N, 10.07; Calculated for $C_{36}H_{16}O_2N_4$ (IV): N, 10.44%.

N, N'-Di (*o*-amino) phenyl-perylenetetracarboxyl-diimide (II).—Red violet powder, insoluble in organic solvents of lower boiling points, sparingly soluble in boiling *o*-dichlorobenzene with violet red color and weak red fluorescence. Conc. sulfuric acid solution shows red violet (thin layer) and red (thick layer) dichroism with strong red fluorescence. The color of the sulfuric acid solution is changed into blue of the imidazoles when heated to 150°. Insoluble in 90% sulfuric acid. Soluble in alkaline hydrosulfite forming violet red vat with weak red fluorescence, from which cotton is dyed in weak dull red violet entirely different form the dyeings of (III). Found: N, 9.56; Calculated for $C_{36}H_{20}O_4N_4$ (II): N, 9.79%.

When the cotton dyeing was diazotized on the fibre and coupled with alkaline β-naphthol the shade was changed into red brown. By heating 1 part of the substance (II) with 200 parts of nitrobenzene at the boiling point for 1.5 hours 57% of the substance converted into Acenaphthene Violet (III) and 43% into the unvattable bis-imidazole (IV). If the boiling is continued for 5 hours the substance is nearly completely converted into the unvattable bis-imidazole.

Condensation of Perylenetetracarboxylic Acid Anhydride with *o*-Nitroaniline.—

N, N'-Di(*o*-nitro)phenyl-perylenetetracarboxyl-diimide (V).—Perylenetetracarboxylic acid anhydride (1.96 g., 1/200 mole) was heated with 6.90 g. (10/200 mole) of *o*-nitroaniline and 1.20 g. (4/200 mole) of glacial acetic acid in an oil bath under reflux with stirring at 230° (bath temperature) for 10 hours. The product was heated up with 50 cc. of alcohol and hot solution filtered. The collected precipitate was then treated with 200 cc. of hot aqueous 1% sodium hydroxide to remove the unchanged tetracarboxylic acid anhydride (recovered anhydride 0.48 g. or 24.4% of the starting material). Yield of (V) is 2.48 g. (78.5% of the theory). Dark brown powder, sparingly soluble in boiling nitrobenzene with red orange color and yellow fluorescence. Soluble in conc. sulfuric acid with strong red fluorescence and red violet (thin layer) and red (thick layer) dichroism. The color of the sulfuric acid solution is not changed into blue by heating to 150° and brown red precipitate is produced by pouring into water. Hydrosulfite vat (IW method) is violet red with weak red fluorescence and cotton is dyed in weak dull red violet, which is identical with the dyeing of the corresponding diamino compound. Found: N, 8.82; Calculated for $C_{36}H_{16}O_8N_4$ (V): N, 8.86%.

Reduction of N, N'-Di (*o*-nitro) phenyl-perylenetetracarboxyl-diimide. — The di (*o*-nitro) phenyl-diimide (V) (1.00 g.) was vatted by heating with 2.0 g. of sodium hydroxide, 2.0 g. of sodium hydrosulfite and 100 cc. of water to 60°, 0.80 g. of 55% sodium sulfide was added and kept further 2 hours at 60°. Water (100 cc.) was then added, oxidized by a current of air, the precipitate collected, thoroughly washed with water and dried at 110°. Yield is 0.84 g. Dark brown powder of violet red streak, soluble in conc. sulfuric acid with red violet (thin layer) and red (thick layer) dichroism and strong red fluorescence. All other chemical and dyeing properties are completely identical with the di (*o*-amino) phenyl-diimide (II) obtained directly with *o*-phenylenediamine. Converted also into Acenaphthene Violet (III) and then into the unvattable bis-imidazole (IV) by boiling with nitrobenzene.

Found: N, 9.45; Calculated for $C_{36}H_{20}O_4N_4$ (II); N, 9.79%.

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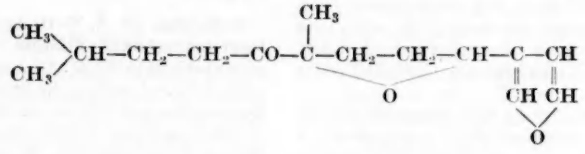
The Bitter Substance, Produced in Black-rotten Sweet Potato. III. On the Constitution of Ipomoeamarone. Part 2.

By Takashi OHNO and Misao TOYAO

(Received May 10, 1952)

It was shown in our previous report[1] that ipomoeamarone was an open-chain sesquiterpenic compound containing a ketonic group, two oxide rings and two ethylenic linkages. It gave a keto-acid (named ceratonic acid) and oxalic acid by oxidation with potassium permanganate at room temperature, and gave acetone, acetic acid, oxalic acid and a liquid



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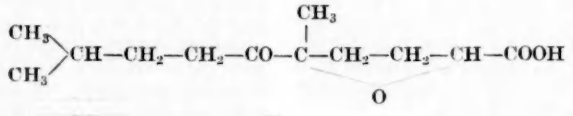

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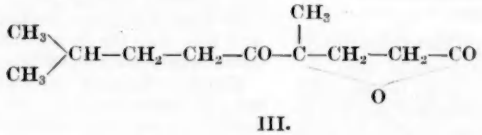
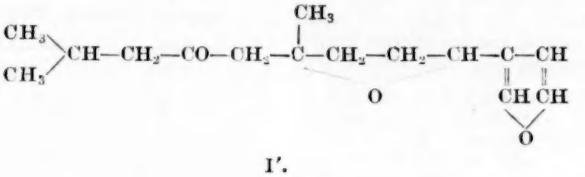
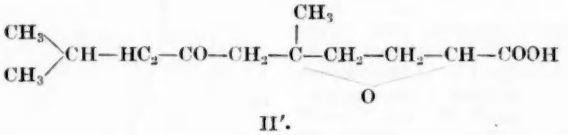


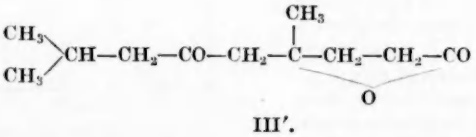
III.



I′.



II′.



III′.

(1) T. Ohno, This Bulletin **25**, 222-225 (1952).

acid by the same oxidation procedure at 100°.

At the general meeting of the Agricultural Chemical Society of Japan, held at Tokyo on April 5, 1952, we proposed tentatively formula I for ipomoeamarone, II for ceratonic acid, and III for the keto-lactone, the latter two of which were the degradation products of the former by oxidation with potassium permanganate.

T. Kubota and his collaborators of the Osaka City College of Polytechnics also announced the results of their own research on ipomoeamarone at the general meeting of the Chemical Society of Japan, held at Tokyo on April 3, 1952, and put forward the formulae of ipomoeamarone (I′), ipomeanic acid (II′) and ipomic lactone (III′), the latter two of which were ozonolysis products of the former.

Some part of their results, including the structures of ipomeanic acid and ipomic lactone, has already been published,[2][3] and their report read at the general meeting of the Chemical Society of Japan was published recently[4].

Though, between Kubota et al. and us, there is an essential disagreement in the interpretation of the structure of ipomoeamarone, we wish to postpone detailed discussion of this and to publish our results read at the general meeting of the Agricultural Chemical Society of Japan as it stands.

As regards the nomenclature of the substances, we think it preferable to use "ceratonic acid", because this name apparently was in print prior to "ipomeanic acid", but we agree with Kubota et al. in adopting the name "ipomic lactone" for the keto-lactone (III or III′).

By oxidation of ipomoeamarone with potassium permanganate at room temperature, a non-volatile liquid acid showing ketonic color reaction was obtained. This was converted into *p*-phenylphenacyl ester (m. p. 79°) and by its analysis a molecular formula, $C_{12}H_{20}O_4$, can be given to the acid. However, neither crystalline semicarbazone nor 2,4-dinitrophenylhydrazone of the acid was obtained. It is now obvious from the results of following experiments that this acid retains the original ketonic and oxidic groups, both present in ipomoeamarone. This acid was named ceratonic acid in our previous paper, and may be identical with the ipomeanic acid of Kubota et al.

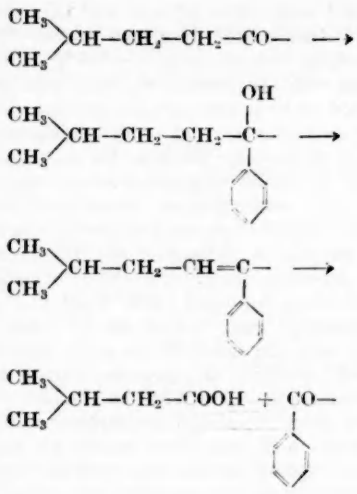
Ipomoeamarone semicarbazone was now oxidized in dilute acetone with potassium permanganate at room temperature, and a crystalline semicarbazone and a mixture of non-volatile liquid acids were obtained. The former was identified with the semicarbazone of ceratonic acid (ipomeanic acid), $C_{13}H_{23}O_4N_3$, m. p. 172°, $[\alpha]_D^{24} = -86.7°$ (in alcohol and pyridine, 4:1). The latter, admixed with some of this crystalline semicarbazone, was then hydrolysed with dilute sulfuric acid in methanol, and fractionated into two parts. The lower boiling fraction (b. p. 99—103°/0.3mm.) coincided with the formula $C_{11}H_{18}O_3$ and was considered to be a keto-lactone, because of its difficult neutralizability at room temperature. It gave positive color reaction for a ketone, but its 2,4-dinitrophenylhydrazone was a liquid and semicarbazone crystallized only partially This lactone was considered to be the ipomic lactone of Kubota et al. The higher boiling fraction, (b. p. 123—135°/0.3 mm.), ceratonic acid, accorded with $C_{12}H_{20}O_4$; *p*-phenylphenacyl ester melted at 79°, and is identical with the ester of the acid, obtained by direct oxidation of ipomoeamarone; the semicarbazone melted at 172° and is identical with the above mentioned semicarbazone. The non-volatile acid was thus proved to be a mixture of ipomic lactone and ceratonic acid.

Ipomoeamarone was treated with phenylmagnesium bromide, and the resulting compound was dehydrated with acetic anhydride and zinc chloride, followed by oxidation with potassium permanganate. Formic, isovaleric, and oxalic acids were obtained besides a non-volatile acid and a lactone.

From the properties of these degradation products obtained by various oxidation methods, it is concluded that: (1) Ceratonic acid is an open-chain acid containing the original ketonic group and one of the original oxide rings, losing three carbon atoms, two ethylenic linkages and an oxide oxygen, and ipomoeamarone possesses therefore, beyond all doubt, a furan-nucleus involving a carbon atom which might have been converted to a carboxylic group of ceratonic acid and three other carbon atoms which might have been lost by oxidation. That is, ipomoeamarone is a furan derivative substituted at α or β position with a side chain of C_{11} which contains a ketonic group and an oxide ring. (2) Ipomic lactone, which is a carbon shorter than ceratonic acid, retains also an original ketonic group, the oxide ring of ceratonic acid being transformed into a lactone ring. The carbon atom of α-position of ceratonic acid may therefore be a

(2) T. Kubota and T. Matsuura, *Proc. Japan Acad.* **28**, 44-47 (1952). They proposed the name "Ipomeamarone" instead of "Ipomoeamarone" for the sake of simplifying the spelling.
(3) T. Kubota and T. Matsuura, Ibid. **28**, 83-84 (1952).
(4) T. Kubota and T. Matsuura, Ibid. **28**, 198-199 (1952).

secondary one, with which oxide oxygen connects, and the oxide ring forms a hydrofuran-nucleus, because the properties of the lactone is considered to be a γ-lactone. (3) The formation of isovaleric acid by the oxidation of the reaction product of Grignard's reagent may establish the constitution of ipomoeamarone to be an isoamyl ketone, and the reaction involved would have taken place in the following manner:



Ipomoeamarone gave dark green color in the pine-shaving test, and an adduct with maleic anhydride, although in a liquid form. In addition, the facts that absorption of hydrogen proceeds only slowly by catalytic reduction, the unsuccessfulness of obtaining dihydro-compound, and the stability of double bonds against sodium ethanolate reduction, are only understood by assuming that two ethylenic linkages of ipomoeamarone form a furan-nucleus.

In consequence, if ipomoeamarone is presumed to be a sesquiterpene derivative and to have a skeleton of an oridinary openchain three-isoprene-structure, such as farnesol or nerolidol, the conclusion may be drawn from the results that ipomoeamarone has a tentative formula (I), ceratonic acid (II), and ipomic lactone (III), respectively.

The only difference between the constitutional formulae of ipomoeamarone of Kubota and of us is the position of ketonic group, and it will be discussed in a future communication.

Experimental

(1) **Ipomoeamarone semicarbazone.**—The yield of semicarbazone by the pyridine-method (see our last communication) from the crude bitter oil was as follows; 60—70 g. of crude semicarbazone from 100 g. fraction 1 (b. p. 140—145°/7 mm.). This product gave 21—25 g. of pure crystals by recrystallization; 80—90 g. of crude semicarbazone from 100 g. fraction 2 (b. p. 145—150°/7 mm.), giving 28—31 g. of pure crystals by recrystallization.

(2) **Hydrolysis of ipomoeamarone semicarbazone.** (a) **By oxalic acid.**—A mixture of the semicarbazone (20 g.) and oxalic acid (30 g.) in water (1 l.) was boiled vigorously for one hour. The product was isolated by means of ether, and ether was washed with aqueous alkali and evaporated. Pure ipomoeamarone (13.6 g.) was obtained by vacuum distillation (yield; 83.4%).

(b) **By potassium bisulfate.**—A mixture of the semicarbazone (5 g.) in benzene (80 cc.) and potassium bisulfate (25 g.) in water (50 cc.) was shaken at room temperature for 175 hours. The benzene layer was separated, washed with saturated sodium bicarbonate solution followed by drying with anhydrous sodium sulfate. After the complete removal of benzene, petroleum ether was added and undecomposed semicarbazone (1 g.) precipitated was filtered off. Free ipomoeamarone was obtained as colorless oil after vacuum distillation of the filtrate; b. p. 112—3°/0.6 mm., $[\alpha]_D^{20} = +11.07°$ (*c*, 2.8 in benzene). (Found: C, 72.24; H, 8.62. Calc. for $C_{15}H_{22}O_3$: C, 72.00; H, 8.80%)

(3) **Oxidation of ipomoeamarone.**—Free ipomoeamarone (2.0 g.), which was regenerated from the semicarbazone, was suspended in water (100 cc.), and powdered potassium permanganate was added to the mixture in small portions under shaking and occasional cooling. After 6 g. of potassium permanganate (corresponding to 7.1 atoms of oxygen) were added, no further decolorisation occurred. Manganese dioxide was then filtered off and washed with hot water. The filtrate and washings were combined, concentrated, decolorized with active charcoal, extracted with ether to remove neutral substances, and acidified with concentrated hydrochloric acid. The separated oil was extrated twice with chloroform, and dried with anhydrous sodium sulfate. A brown viscous acid (1.6 g.) was obtained after the removal of chloroform. The liquid acid showed positive color reaction for ketone with sodium nitroprusside, although it gave no crystalline semicarbazone. Its *p*-bromophenacyl ester was liquid, but *p*-phenylphenacyl ester was obtained as leaflet crystals mixed with oily substance, m. p. 79° from alcohol. Analysis showed that the ester corresponds to the formula $C_{26}H_{36}O_5$, showing that the acid is $C_{12}H_{20}O_4$. (Found: C, 73.43; H, 6.98. Calc. for $C_{26}H_{36}O_5$: C, 73.94; H, 7.11%)

It is obvious that the acid, as shown in the next experiment, preserves the original ketonic

group and one of the oxide rings, and we proposed the name ceratonic acid to this acid in our previous paper. It may be the same compound as the ipomeanic acid of Kubota et al.

The aqueous layer, separated from chloroform solution, was neutralized with aqueous ammonia, and a solution of calcium chloride was added to it. Calcium oxalate was precipitated; 0.16 g. (namely 0.16 equivalent).

(4) Oxidation of ipomoeamarone semicarbazone.—To a solution of ipomoeamarone semicarbazone (20 g.) in acetone (200 cc.), treated beforehand with potassium permanganate, water (200 cc.) was added, followed by the addition of powdered potassium permanganate in small portions under shaking and occasional cooling. Forty-seven grams (equivalent to 6.85 atoms of oxygen) were consumed. After manganese dioxide was decomposed by passing sulfur dioxide gas through the reaction mixture, it was concentrated to half its volume under diminished pressure, and inorganic substances were filtered off and washed with ether. The filtrate was extracted repeatedly with ether, the combined ether extract was washed with 10% sodium hydroxide solution repeatedly, and 3.6 g. of a neutral oil, which crystallized immediately, was obtained after evaporation; colorless powder, m. p. 119° (from ether and petroleum ether). Mixed melting point determination and analytical value showed that it was the unreacted semicarbazone. (Found: C, 62.78; H, 7.98; N, 13.48. Calc. for $C_{16}H_{25}O_3N_3$: C, 62.54; H, 8.14; N, 13.68%)

Aqueous layer mixed with sodium hydroxide solution was acidified with dilute sulfuric acid, fractionating into a part soluble in ether and crystals soluble in ether with difficulty. The latter was ceratonic acid semicarbazone; colorless powder from ether, m. p. 172° (decomp.), $[\alpha]_D^{24}$ = −86.7° (*c*, 6.0 in ethanol and pyridine, 4:1). (Found: C, 54.81, 54.51; H, 8.57, 7.94; N, 14.97, 14.73. Calc. for $C_{15}H_{25}O_4N_3$: C, 54.74; H, 8.07; N, 14.74%) The former was a viscous liquid (11 g.) admixed with some crystals of the semicarbazone. The oil was refluxed with 25% sulfuric acid (50 cc.) in methanol (100 cc.) for 3 hours, the methanol was removed, and the separated oil was extracted with ether and the ether extract distilled in a vacuum. A viscous oil (6.6 g.) was obtained; b. p. up to138°/0.15 mm., $[\alpha]_D^{20}$ = +18.0° (*c*, 2.0 in ether). *p*-Phenylphenacyl ester melted at 79°, which was identical with the ester above mentioned, was contaminated by an oily substance; no crystallien semicarbazone was obtained. By analysis of the acid it was shown to be a mixture of two substances, $C_{12}H_{20}O_4$ and $C_{11}H_{18}O_2$. (Found: C, 64.54, 64.24; H, 9.59, 9.19. Calc. for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Calc. for $C_{11}H_{18}O_2$: C, 66.67; H, 9.07%.)

The mixture of the acid (5.0 g.) was fractionated as follows: (A) b. p. 99—103°/0.3 mm., 2.5 g., (B) b. p. 103—123°/0.3 mm., 0.5 g., (C) b. p. 123—135°/0.3 mm., 1.5 g. The first fraction, a pale yellow mobile oil, was considered to be a lactone, because it was neutralized with N/10 potassium hydroxide solution only when warmed. *p*-Phenylphenacyl ester was not obtained. The first and second fraction in ether were treated with sodium bicarbonate solution to remove acidic substances if any, and the lactone was obtained by shaking it repeatedly with 10% sodium hydroxide solution, followed by acidifying, extracting with ether, and distilling in vacuo, b. p. 134—140°/4 mm., 1.0 g. (Found: C, 67.01; H, 9.00. Calc. for $C_{11}H_{18}O_2$: C, 66.76; H, 9.09%)

The lactone gave a color reaction with sodium nitroprusside, but the semicarbazone was crystallized only partially. The 2,4-dinitrophenylhydrazone remained oily; yellow crystals, which were formed in an alcoholic solution by cooling with a mixture of dry ice and ether, melted at room temperature. This ketolactone may be the same compouud as the ipomic lactone of Kubota et al.

The third fraction, a viscous yellow oil, proved to be ceratonic acid. The acid was converted into *p*-phenylphenacyl ester, m. p. 79° and also into semicarbazone, m. p. 168° (decomp.); these proved to be identical with the derivatives which were mentioned above, respectively. Analysis of the oil corresponds to $C_{12}H_{20}O_4$. (Found: C, 63.20; H, 8.69. Calc. for $C_{12}H_{20}O_4$: C, 63.16; H, 8.78%)

(5) Reaction of phenylmagnesium bromide upon ipomoeamarone and oxidation of the product by potassium permanganate.—To an ice-cooled solution of ipomoeamarone (5.6 g., regenerated from the semicarbazone) in ether was added a solution of phenylmagnesium bromide in ether (2.7 N, 15 cc.) dropwise and the mixture was refluxed for 30 minutes. The reaction product was poured into a mixture of ice and dilute sulfuric acid. The ethereal layer was separated, washed with saturated bicarbonate solution, and dried. To the viscous product obtained by removal of the ether, 4 g. of acetic anhydride and a small portion of zinc chloride were added. After refluxing for 30 minutes, the mixture was poured into water. Ether was added, washed with 10% potassium hydroxide solution and dried. The removal of the ether left 6 g. of a viscous dark-brown oil.

The oil obtained was oxidized with potassium permanganate in dilute pyridine (100 cc. pyridine and 300 cc. water). Thirteen grams of potassium permanganate were required (corresponding to 6.8 atoms of oxygen). Manganese dioxide was now removed by filtration and washed with hot water. From the filtrate and washings pyridine was distilled off with steam. The residual solution, after concentration to half its volume, was treated with ether to remove non-volatile neutral substances (0.1 g.), and the aqueous layer was distilled with steam after acidification. The distillate was neutralized and treated with potassium permanganate solution for decomposition of formic acid. The filtrate from manganese dioxide was concentrated to dryness, acidified, and extracted with ether. The volatile acid (250 mg.) was converted to *p*-bromophenacyl ester, m. p. 64°. This was proved to be the ester of isovaleric

acid by mixed melting point determination and analysis. (Found: C, 52.00; H, 5.60. Calc. for $C_{13}H_{15}O_3Br$: C, 52.17; H, 5.02. Calc. for $C_{12}H_{13}O_3Br$: C, 50.53; H, 4.56%) The mixed melting point with the ester of isobutyric acid showed a depression of about 10°.

From the residual solution of steam-distillation, there were obtained a non-volatile acid (0.9 g.), a lactone (0.1 g.) and oxalic acid.

Summary

By oxidation of ipomoeamarone and its semicarbazone with potassium permanganate, ceratonic acid (ipomeanic acid) (II), $C_{12}H_{20}O_4$, and ipomic lactone (III), $C_{11}H_{18}O_3$, were obtained. The ketonic group of ipomoeamarone was proved to be an isoamyl ketone by the oxidation of the reaction product of Grignard's reagent. These experiments led us to conclude that ipomoeamarone is represented by the provisional constitution (I).

We wish to express our sincere gratitude to Prof. S. Takei and Dr. M. Ohno of the University of Kyoto for their guidance and to Dr. M. Matsui of our Laboratory for his helpful advice given to us during our research.

Nissin Chemical Co., Osaka Works, Osaka

Additions and Corrections

Volume 24, 1951

S. Shida and S. Fuzii. Calculation of the Diamagnetic Anisotropy of Benzene by the Method of Antisymmetric Molecular Orbitals.

Page 244. In formula (14) for "R'_2" read "R'_4".

Page 245. In table I, "$R'_2=0.0318$ for" read "$R'_4=0.318$"

M. Mori. On Some Dark-colored Chloroplumbates (II, IV) of the Type $[M^{III}A_6]PbCl_6$.

Page 286. In col. I, line 55, for "sallow" read "shallow". In col. 2, line 7, for "$Co(NH_3)_6$" read "$Co(NH_3)_5$"; for "H_2O-PbCl" read "H_2OPbCl"; line 34, "Pb, 36.00" read "Pb, 36.00%"; line 49, "Gouy's cylinder..." read "the Gouy cylinder ..."; in foot-note, "Chem. Abst. 34" read "Chem. Abst, 35"

Page 287. In col. 2, in foot-note, "$[Co(NH_3)_6](Pb^{II}Cl_6)(Pb^{II}...$" read "$[Co(NH_3)_6]_3(Pb^{II}...$"

Volume 25, 1952

K. Sone. Spectrochemical Studies on the Anomalous Color Reactions of Some Iron (II) Chelate Compounds.

Page 1. In col. 2, line 2 under Fig. 1,

Page 2. In col. 1, line 12; line 14 and in col. 2, line 7 from bottom, for "a ferrous ion" read "ferrous ion"

Page 3. In col. 1, line 6 from bottom, "a visible band" read "the visible band".

K. Murata. Synthesis of 2-Amino-4-methyl-5-cyanothiazole from Acetonitrile.

Page 17. In col. 2, line 11 for "Sodio-β-..." read "sodium-β-..."; line 19, for "Receystallized" read "Recrystallized"; line 3 from bottom, for "fitlered" read "filtered".

M. Muramatsu and T. Sasaki. On the Nature of Built-up Film. I. & II.

Page 24. In col. 1, line 32, for "from echion" read "from echelon"; line 48 & Page 25. In col. 2, line 1, for "from water the surface of water" read "from the surface of water".

H. Inokuchi. The Electrical Conductivity of Condensed Polynuclear Aza-aromatic Compounds.

Page 31. In col. 1, bottom, for "Indanrthazine" read "Indan-thrazine".

Page 32. In col. 2, line 2, for "resis & tivity" in changing line should be connected by hyphen.

M. Tamura and M. Kurata. On the Viscosity of Binary Mixture of Liquids.

Page 38. In col. 1, line 3 for "we can put(2)" should be "we can put(12)".

T. Isemura and K. Hamaguchi. Surface Chemistry of Synthetic Protein Analogues I.

Page 41. In col. 1 line 23, for "pyrididine" read "pyridine".

Page 42. In col. 2, in Fig. 5, for "Effect of substrate on the acidity of monolayer" read "Effect of acidity of substrate on the monolayer of".

Y. Shimura. The Relation between the Geometrical Configuration of Inorganic Complexes and their Absorption bands. II.

Page 48. In col. 1, in table 2, line 1, for "Sulfitoo-" read "Sulfito-", in same table, line 7, "Sulfon-" read "Sulfono-".

Page 49. In col. 1, line 14, for "because" read "became".

Y. Shimura. The Relation between the Geometrical Configurations of Inorganic Complexes and their Absorption Bands. III.

Page 50. In col. 2, line 13, for "sulfon-" read "sulfono-".

Page 52. In col. 2, line 39, for "second are" read "second bands are".

Page 53. In col. 1, line 25, for "$[Co(NH_3)_4HO_2\cdot Cl]Cl$" read "$Co(NH_3)_4H_2O\cdot Cl]Cl$", line 30, for "$[Co[NH_3)_4$" read "$[Co(NH_3)_4$", line 33, for "$[Co(NH_3)_4NO_2\cdot NCS]Br\cdot N_2O$" read "$[Co(NH_3)_4NO_2\cdot NCS]Br\cdot H_2O$".

Page 53. In col. 2, line 3, for "trans-$[COen_2NO_2\cdot$" read "trans-$[Co\ en_2NO_2\cdot$"

T. Nishimura. Antituberculous Compounds. I.

Page 55. In col. 1, line 29, "$-5-10°$" read "$-5\sim-10°$".

T. Ando, J. Ito, S. Ishii and T. Soda. A Note on the Identification of Ortho-, Meta- and Pyrophosphates by Means of Paper Chromatography.

Page 78. In col. 1, line 8 from the bottom, for "Ishi" read "Ishii". In col. 2, line 13 from the bottom, "usefull" read "useful".

Page 79. In col. 1, line 21 from the bottom, "No," read "No."; line 13 from the bottom, for "by spot Tests" read "by Spot Tests".

M. Kashima. Molecular Structure of Monochloromethyl Chloroformate.

Page. 79. In col. 1, foot-note, "O. Gorman" read "O'Gorman". In col. 2, line 6 from the bottom, "Y. Kuwata" read "T. Kuwata". line 1 for "conclusiosn" read "conclusions"; line 20, "$R-C(O^-)(O-R)$" read "$R-C(O^-)(O^+-R)$"

S. Kikuchi, Y. Sakaguchi and K. Honda. Pen Writing Polarograph with Direct Current Amplifier. Page 100. In Table 1, In $E_{1/2}$ (photographic) column, for "-0.229" read "-0.129".

M. Tamura and M. Kurata. On the Viscosity of Solutions of Non-electrolytes.

Page 126. In col. 2, line 17, for "against 1/T" should be "against $1/T^{(?)}$.".

S. Yamada and R. Tsuchida. Spectrochem. Study of Microscopic Crystals. II.

Page 128. In col. 1, line 17, for "each of the absorptions" read "the two absorptions".

R. Senju. Eine neue Bestimmungs methode von Ligninsulfosäure in Sulfitablauge.

Page 131. In title of table 1, for "Kunstseide Sulfit Zellstoff-Fabrik" read "Kunstseidesulfitzellstoff-Fabrik". in final part, for "Universitōt" read "Universität".

H. Suzuki. The Spatial Configurations and the Ultraviolet Absorption Spectra of Stilbene Derivatives.

Page 146. In col. 2, line 32, for "$-\beta g$ and $+\beta$" read "$-\beta$ and $+\delta$". line 17, for "othylenie" read "ethylenie".

M. Izawa. Monolayers of Branched-Chain Fatty Acids. I.

Page 185. In col. 1, in Fig. 4 "1, II, III" read "VII, VIII, IX".

S. Akabori, K. Ohno and K. Narita. On e Hydrazinolysis of Proteins & peptides.

Page 214. In col. 2, line 7, for "aware of hydrazinolysis" read "aware of, hydrazinolysis".

Page 217. In col. 2, line 2 from bottom, for "soveral" read "several".

Y. Namba and T. Oda. X-Ray Investigation of Trimethylacetic Acid Crystal.

Page 225. In title, for "Tsutom" read "Tsutomu", in reference (6), for "T. Watanabe" read "T. Watanabé"; in final part, for "*Chenical Laboratory Osaka Liberal*". read "*Chemical Laboratory, Osaka Liberal*".

I. Iwasaki, S. Utsumi and T. Ozawa. New Colorimetric Determination of Chloride using Mercuric Thiocyanate & Ferric Ion.

Page 226. In col. 2, line 32, for "cyanide, thiosulfate &" read "cyanide, sulfide thiosulfate &"; line 50, for "to the detrmination of" read "to the determination of"; line 51, for "in water" read "in waters".

S. Fukusima, A Study on the Mechanism of Catalytic Action of Manganese Dioxide on the Decomposition of Potassium Chlorate by Use of Heavy Oxygen as an Isotopic Tracer.

Page 245. In col. 2, line 15, for "had been whose increased" read "had been increased".

Page 248. In col. 1, in table 2 "$(m\mu)$" read "(μ)".

K. Nakamoto. Dichroisms of Benzene Rings III.

Page 256. In Col. 1, line 32, for "*m*-dinitroboenzene" read "*m*-dinitrobenzene".

Page 257. In col. 2, lines 12, 25, 37, for "hypsochromic" read "hyperchromic".

M. Izawa. Monolayers of branched-chain fatty acids II.

Page 314. In col. II 2, at the bottom, for "...14, 16." read "...14, 15."

S. Fujiwara. Formula for the Melting Points f Inorganic Compounds of Type MXO_n.

Page 348. In Table 1, α_+ of K^+, for "0.29" read "0.9".

Page 349. In col. 2, line 2 from the bottom, for "showing the linearity functions" read "showing the linearity of the functions".

Y. Tanito, Y. Saito and H. Kuroya. The Crystal Structure of "Dichlorochloride" $[Co(NH_3)_3H_2OCl_2]Cl$.

Page 328. In col. 2, line 8 from the bottom, for "[10$\bar{1}$0]" read [100]; line 7 from the bottom for "[11$\bar{2}$0]" read "[120]".

Page 331. In col. 1, line 3, for "eads" read "lead".

A. Nakahara, Y. Saito and H. Kuroya. The Crystal Structure of Trans-dichloro-diethylenediamine-cobalt. III.

Page 331. In title, for "...cobalt. (III). chloride" read "...cobalt (III) chloride".

Page 333. In Table 2, In the top of right column, for "$E_{calc.}$" read "$F_{calc.}$".

I. Yasumori. On the Binding Energy of LiH.

Page 358. In col. 1, line 2 for "energy'" read "energy". In col. 2, line 15 for "0.71" read "0.17"